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Conversion of Cattle Feedlot Manure to Ethylene and Ammonia Synthesis Gas

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TO ETHYLENE AND AMMONIA SYNTHESIS GAS

by

William J. Huffman
James E. Halligan
Roger L. Peterson
Texas Tech University
Lubbock, Texas 79409

Grant No. S-802934

Project Officer

R. Douglas Kreis
Source Management Branch
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ADA, OKLAHOMA 74820

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FOREWORD

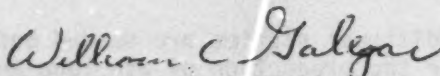
The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's endeavors to fulfill its mission involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured. The primary and ultimate goal of these efforts is to protect the nation from the scourge of existing and potential pollution from all sources.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report is a contribution to the Agency's overall effort in fulfilling its mission to improve and protect the nation's environment for the benefit of the American public.



William C. Galegar, Director
Robert S. Kerr Environmental
Research Laboratory

ABSTRACT

An investigation was undertaken to scale-up a partial oxidation reactor to evaluate the potential for producing an ammonia synthesis gas from cattle feedlot residue. Because conventional ammonia production involves a commercial process which produces an intermediate synthesis gas from natural gas, air, and water, the only part of the total process that needed to be investigated was the reactor system. The synthesis gas from the reactor can be further processed to produce ammonia using existing, commercial technology.

During this phase of the study, a nominal 2.5 meter (m) long, falling-bed reactor was designed, constructed, and operated along with supporting feed and recovery equipment; manure feed rates to the reactor ranged from 7.7 to 23.6 kilograms per hour (kg/hr). The results show that significant yields of an ammonia synthesis gas and ethylene can be produced in the same reactor when the system is fed with a mixture of air, steam, and manure. This study and earlier bench-scale experiments (EPA-660/2-74-090) show that the product gases are compatible with both ethylene and ammonia synthesis gas production. The maximum production rates were not encountered during the investigation; however, the experimental data and earlier results show that the ammonia equivalent of manure is in excess of one-half metric ton of ammonia per metric ton of dry, ash-free manure. The production of ethylene ranged from 21 to 70 grams per kilogram (g/kg) of dry, ash-free manure; production rates up to 80-90 g/kg may be possible pending further studies on reinjection of liquid products. The process has been developed assuming that manure contains about 15 percent moisture and 25 percent ash.

The production of ammonia synthesis gas from cattle feedlot manure is recommended for scale-up to a pilot demonstration unit using the technology developed here and that used for general solid waste processing.

Additional studies are needed before a complete design can be specified for the production of ethylene and other petrochemical intermediates. The development of this technology could have a significant impact on the feedstock supply for the petrochemical industry and should, therefore, be vigorously pursued at the current scale and during the operation of the recommended pilot demonstration unit for production of ammonia synthesis gas.

This report was submitted in fulfillment of Grant No. S-802934 by Texas Tech University under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 1, 1974, to June 30, 1977, and work was completed as of June 30, 1977.

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SECTION I

INTRODUCTION

The cattle feedlot industry in the United States supplies a high-volume, beef consumer market as indicated by the sales of nearly 25 million head of feedlot cattle in 1972.¹ This beef consumer market demands a high-volume industry at all times despite the rather wide and severe fluctuations that do occur, and seem to be the rule rather than the exception. Both the high volume and fluctuations are illustrated by the production cycles recorded within the service area of one utility company in West Texas: approximately 4 million head were fed-out in 1974² compared to nearly 5 million head in 1973;³ actual production in 1975 may be less than 3.5 million.⁴

The most negative aspect of feedlot operations is the solid by-product, cattle manure, which can harm the environment by water run-off into watersheds and by noxious gas emitted into the atmosphere.⁵ When cattle are fattened by grazing, the large area of land involved dilutes the potential effect of pollution; but, a concentration of potential problems is, by definition, associated with feedlots. Land spreading, still the most used method of manure management,⁶ cannot be economically attractive when large quantities of the by-product must be trucked any distance to achieve only dilution (\$2.25 per ton charge for ten-mile haul has been estimated by Sweeten⁷). As a result, huge piles of cattle feedlot manure accumulate.

This accumulation has been accentuated in recent years because there is a trend toward larger feedlots, even with the severe cycles that the industry experiences. For example, within the utility service area noted above, 127 feedlots produced 1.2 million head of cattle in 1966; 188 feedlots produced 3.7 million head in 1970; and 150 feedlots produced 4.1 million head in 1974. In the Hereford-Dimmit area on the High Plains of Texas, the estimated production of 30 or fewer lots is 800,000 - 1,000,000 cattle.⁸

The concentration and accumulation of cattle feedlot manure is currently an undesired by-product of the industry, but it may also be viewed as a "residual resource," particularly in terms of the energy deficiencies projected for Texas and the United States. Proceeding on the assumptions that the environment must be protected and that a productive end-use can be developed for this resource, one immediately asks, "What are the technical options? How much do they cost? Can a profit be realized?"

Several technical options for using this by-product of the industry have been considered by a number of investigators. These options include, but are not necessarily limited to: a) utilization for land fertilizer;^{9,10} b) direct combustion (either singly or combined with solid fossil fuel)

for energy value;¹¹ c) feed ingredient in cattle rations;¹⁰ d) synthesis gas generation by anaerobic digestion;¹² e) synthesis gas by pyrolysis or partial oxidation;¹³ and f) production of single cell protein.¹⁴

The economics of these options for cattle feedlot manure and their possible use for general biomass utilization have been considered by many groups and individuals as a means of supplementing food and energy supplies. The evaluations include those of Boersma and Barlow,¹⁵ Elias,¹⁶ Inst. Gas Technology, and U. S. Energy Research and Development Administration,¹⁷ Heichel,⁹ Chancellor and Goss,¹⁸ Whetstone,¹⁹ Parker and Whetstone,²⁰ Sweeten,¹⁰ Halligan and Sweazy,²¹ and Engler, et. al.²² This listing and the previous one on technical options are not intended to be all inclusive; instead, references are cited only to show the breadth and diversity of interest in virgin and residual biomass utilization. The general results of these investigations and evaluations suggest that the technical feasibility and economics of the options for cattle feedlot manure are comparable to that for the utilization of municipal solid waste (excluding direct combustion) as indicated by Halligan and Huffman.²³ Using the incomplete, but more reliable results available from municipal solid waste demonstration projects,¹¹ one can project that similar processes for cattle feedlot manure utilization are quite probably viable providing the volume of waste processed within a radius of 50 miles exceeds 750 tons per day, a viable, high volume, local market exists for the conversion product, and long-term (10-20 years) investment financing can be obtained. Without long-term financing, one must, however, conclude that the processing and utilization of huge volumes of cattle feedlot manure is, at best, a marginal investment at this time in history. In other words, potential investors in supplemental or alternate energy source projects soon learn that oil and gas are still highly attractive energy sources. It is reasonable to expect that oil-equivalent prices will probably have to exceed \$15-18 (in 1975 dollars) before several of the aforementioned alternates become truly profitable for private investments. These marginal alternates include those which depend upon biological action or high solids residence time (> 30 min).¹²

It is very important to note that none of the cited evaluations have placed or would have placed a dollar value on the aesthetics of removing manure and other solid residues (residual biomass) from the environment. We doubt that one can assign a value; but, one must carefully consider this qualitative aspect. For the short-term development of such processes, the importance of pollution abatement may well be the crucial one instead of the need for alternate energy supply. This concept has been summarized by Whetstone¹⁹ as follows: "... much of the cost in the conversion of wastes to energy may be legitimately charged to pollution control; all of the cost of biomass crops must be borne by the energy and other values obtained . . ." (emphasis by Whetstone). Alternately, as one of us (JEH) has noted: solid residues are not an answer to the energy crisis; the energy crisis may well be the answer to the solid residue disposal problem. Thus, one may project that pollution abatement may provide a key motivation factor for developing energy processes based on biomass. The improvements evolved from such processing may then lead to highly competitive energy processes based on biomass feedstocks.

The preceding discussion strongly indicates that research on the utilization of cattle feedlot manure is justified, particularly in terms of pollution abatement. The question is then what option. Certainly, investigations on a number of options must be carried far enough to provide a sufficient data base for realistic economic comparisons. This report presents the results on one option which is consistent with the preceding economic projections: the thermochemical processing or partial oxidation of cattle feedlot manure for high-volume production of ammonia synthesis gas. The technical basis for this research has been reviewed in a number of publications by Halligan and his colleagues^{13,21,24,25,26} and will not be recounted here; the reader is requested to refer to these publications, particularly reference numbers 13, 24, and 25.

The rationale for choosing to investigate and develop thermochemical processing and specifically the production of an ammonia synthesis gas was and is as follows. Large numbers of cattle are concentrated in feedlots and these animals require many thousands of acres of land in grain crops. In turn, these crops demand significant quantities of fertilizers for efficient production, such as anhydrous ammonia.²⁴ As a result, large ammonia plants (500-1000 tons per day) are not uncommon in the vicinity of extensive, fed-cattle operations such as those in Texas, California, Colorado, and Arizona.

Most of the ammonia produced in the United States is based on reforming natural gas with steam to produce the hydrogen-nitrogen mixture required for ammonia synthesis.²⁷ Because of the projected, critical shortage and/or higher price levels of natural gas, many ammonia producers are investigating the replacement of natural gas with other hydrogen sources.²⁸ Obviously, the utilization of cattle feedlot manure would not eliminate the need for natural gas in ammonia production, but the interdependence of ammonia production and feedlots via feed grain does strongly suggest that some natural gas replacement may certainly be expected, upon development of an economical process.

It is important to note that, during the course of this project, the investigators have received serious contacts from more than six private firms relative to commercialization; two of the firms are continuing their analyses and discussing a joint venture. Several of these contacts have developed from the joint public announcement issued by the U. S. Environmental Protection Agency, Pioneer Corporation, Texas Cattle Feeders Association, and Texas Tech University on July 29, 1975.

SECTION II

CONCLUSIONS

1. The 2.5 m long reactor used in this study demonstrated that a partial oxidation reactor for producing an ammonia synthesis gas can be scaled-up from 0.1-0.4 kg/hr to 7.7-23.6 kg/hr of as-received feed using reaction temperature as the correlation parameter. Heat transfer to particles appears to be the controlling factor for scale-up considerations.
2. The investigation has shown that 21-70 g/kg of ethylene can be produced using the reactor design and operation that evolved during the course of the investigation. The production of this valuable olefin depends upon reaction temperature and the time-temperature history of the solids-gas in the reactor design as operated.
3. Limited energy/material balances were insufficient to demonstrate that the reactor can be operated adiabatically. The results were, however, sufficient to show that the large, 2.5 m long reactor was similar to the small bench-scale unit. Thus, reactor char (approximately 35 percent of the total dry mass containing 50-55 percent ash; heat value approximately 3,300 calories per gram (cal/g) would have to be consumed within the process to generate steam and/or compensate for sensible heat effects.

SECTION III

RECOMMENDATIONS

1. A reactor process for the production of an ammonia synthesis gas should be scaled-up to a pilot demonstration unit which is capable of processing 200-300 ton per day of as-received cattle feedlot manure (15-30 percent moisture, 20-25 percent ash by weight). Because a final design will require approximately one year to prepare, from date of acceptance of this report, it is anticipated that the additional data needed to confirm energy balances could be available from the current reactor for critical design considerations. These data are currently being obtained as part of an United States Energy Research and Development Administration Contract with the Fuels From Biomass Program, Division of Solar Energy (Contract No. E(29-2)-3779).

This recommendation is based upon the generally positive results of this study. It is strongly urged that this recommendation be given serious consideration to help demonstrate to the important agricultural sector of this country that positive, technical advances can and are being made to help alleviate their rising, energy-related costs and investments through the use of a neglected solid residue resource.

2. Investigations at the current reactor scale should be continued to specify energy and material balances and help define the factors that control the production of ethylene and other valuable petrochemical intermediates. Studies should also be initiated to evaluate the feasibility and desirability of reinjecting product tar and liquid into the reactor to increase hydrocarbon yields.
3. Basic studies should be initiated to develop a firm understanding of the residence time-history of the reactor design-operation that evolved during the investigation. These studies could provide valuable information relative to the use of other solid wastes and feedstocks.
4. A development program should also be undertaken to assess the effect of reaction pressure on product yield. This study could be initiated on a small, bench-scale unit because the effect of reaction temperature on scale-up has been established for the production of an ammonia synthesis gas. The effect of pressure up to 30 atmospheres (atm) should be investigated to provide a crucial data base for selecting economic optimums. This study could also be incorporated into the first recommendation.

5. Because the volume of cattle feedlot residue fluctuates rapidly from year to year, immediate studies should be initiated to evaluate the use of other agricultural waste products as feedstocks for the reactor process. This would stabilize the supply of feedstock and reduce the investment risk.
6. Studies should be initiated to define better the end-uses of the final, ash product from the process; to determine the pollution potential of the final wastewater stream and the potential recovery of organics contained therein; and to determine the stack emissions during combustion of the product tar.

SECTION IV

SGFM PROCESS DESCRIPTION

The current scope of the Synthesis Gas From Manure (SGFM) process is one which is projected to produce an ammonia synthesis gas (Nitrogen + Hydrogen) and ethylene (a key chemical feedstock) from the solid by-product of commercial feedlots. A block diagram of the overall process that is projected for a full-scale plant is shown in Figure 1. In Figure 1, it must be appreciated that complex chemical processing is involved in each block, except for Feed Preparation and Energy Recovery where standard equipment and combustion units would be employed.

The heart of the process is the reactor section which utilizes high temperature to decompose the solid feed into useful gas products for sales. A solid char (approximately 3300 cal/g) and an organic liquid are also produced but these will be used internally. The solid char will be needed to provide certain utility needs, e.g., generation of steam. The liquid product will be recycled to the reactor to assure that the hydrocarbon content of the gas can be achieved and/or combusted to recover its energy content.

After production in the SGFM process, the ammonia synthesis gas could be fed to an existing ammonia plant as a replacement for part of the natural gas feed, or other feedstock that might be used. The ethylene could be transported and sold to a petrochemical company using an existing pipeline; the pipeline transport may require that the ethylene be blended with another gas. Thus, in terms of this scope, the SGFM process would be located near an existing ammonia plant with close access to an existing pipeline. Our current information indicates that these criteria can be met in the Hereford-Dimmit area of West Texas. Other locations could be chosen on the basis of local market needs for ammonia synthesis gas, low BTU gas and/or ethylene. Other product options are also being considered by the investigators.

As indicated above, the heart of the process is the reactor design and operation. Other items in the process are already commercially available and do not require additional development. Thus, this project has concerned itself with reactor development.

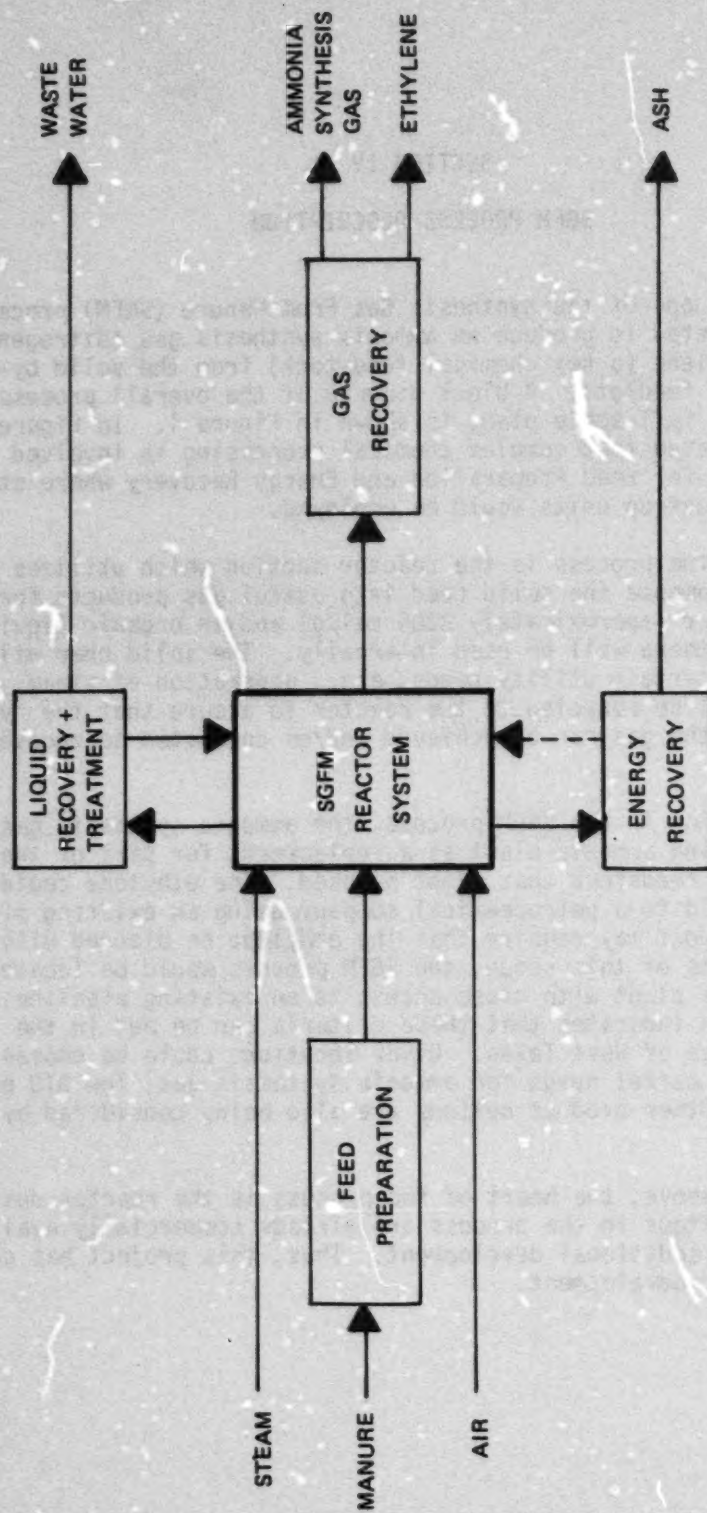


Figure 1. General flow sheet for the SGFM process.

SECTION V

EXPERIMENTAL EQUIPMENT, PROCEDURES AND MATERIALS

As with most developmental projects, the equipment and procedures were in a constant state of change throughout the course of the project. As more data became available on the operating characteristics of the system, various modifications were initiated to increase reliability, improve the accuracy, remove limitations, and enhance understanding of the data. The material presented in this section incorporates the original and latest revisions to illustrate difficulties in working with hot solids and gases. Characterization data on cattle feedlot manure are given in reference 24.

FLOW OF FEED AND PRODUCT COMPONENTS

Solid manure was fed to the top of the hot reactor where it fell countercurrent to a gas mixture of steam and air which were introduced through a distribution plate at the bottom. Gases resulting from the pyrolysis and partial oxidation of the manure exited with the input gas stream out the top of the reactor. The gas was stripped of entrained solids, tars, and condensables in stages. Char was removed from the bottom of the reactor through an opening in the input gas distribution plate. This flow path scheme is illustrated in Figure 2.

REACTOR AND FEED HOPPER

The reactor was made from schedule 40 stainless steel pipe, Figure 3. The main body of the reactor consisted of a 15.24 cm diameter, 1.524 m long section at the top for separation of the solids and gas. In order to allow for approximately 2 cm vertical expansion due to the high temperature operation, the reactor was welded to horizontal, 20 cm I-beams at the bottom and guided at the top by triangular ears which moved in slots welded to another set of I-beams.

A star feeder, Model R2-653 manufactured by Beaumont Birch Co., was mounted between the manure hopper and the reactor using a Reliance VSD variable speed motor, Model B56G3102, with a 12 to 48 sprocket gear ratio.

The inlet gas distribution plate at the bottom of the reactor consisted of a 0.95 cm stainless steel plate with concentric circles of 0.1588 cm holes drilled into it around a 2.54 cm hole in the center. This distribution plate was welded to a thin collar which was welded to the bottom flange of the reactor to provide an even distribution of gas to the bottom of the

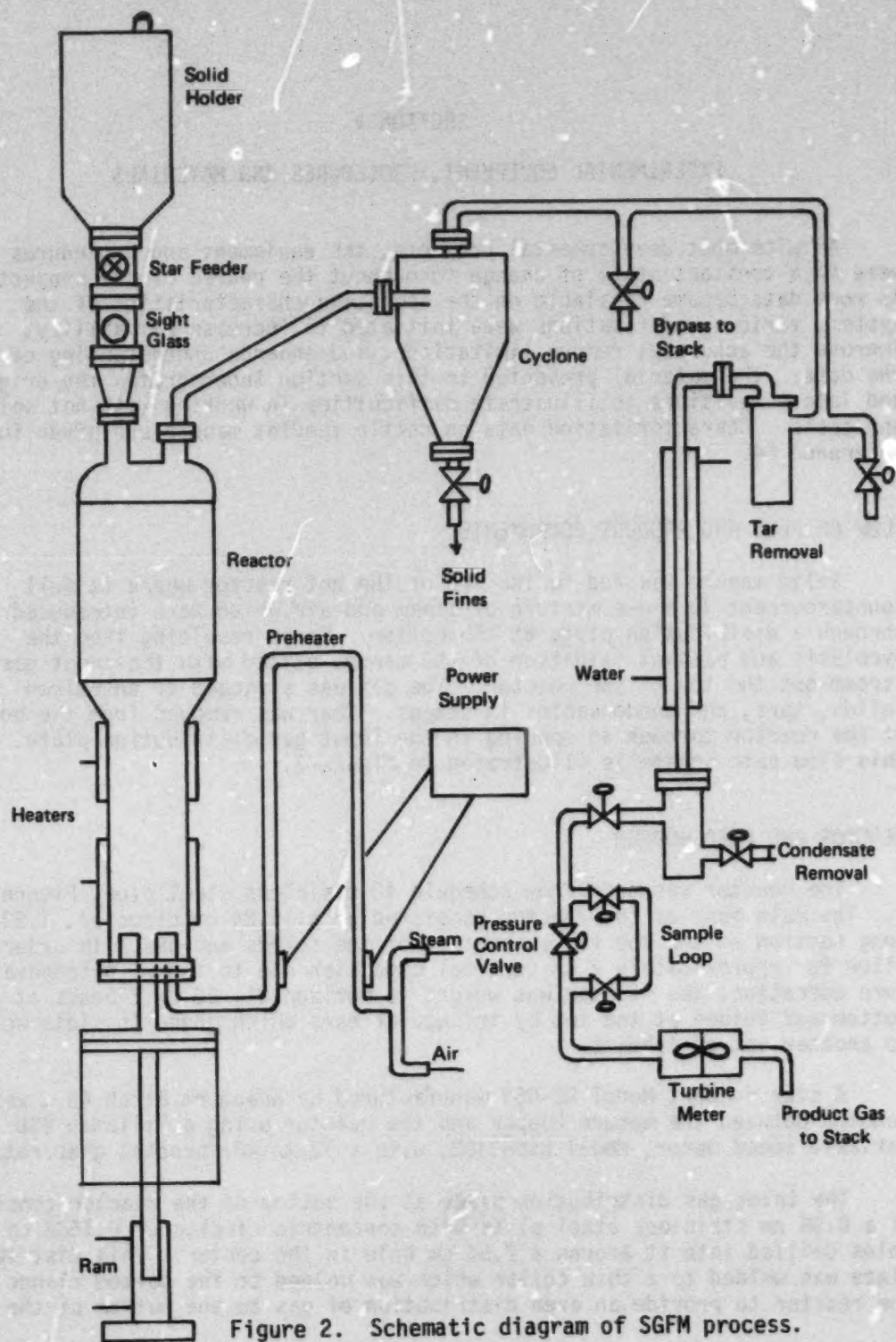


Figure 2. Schematic diagram of SGFM process.

(All Dimensions in Centimeters)

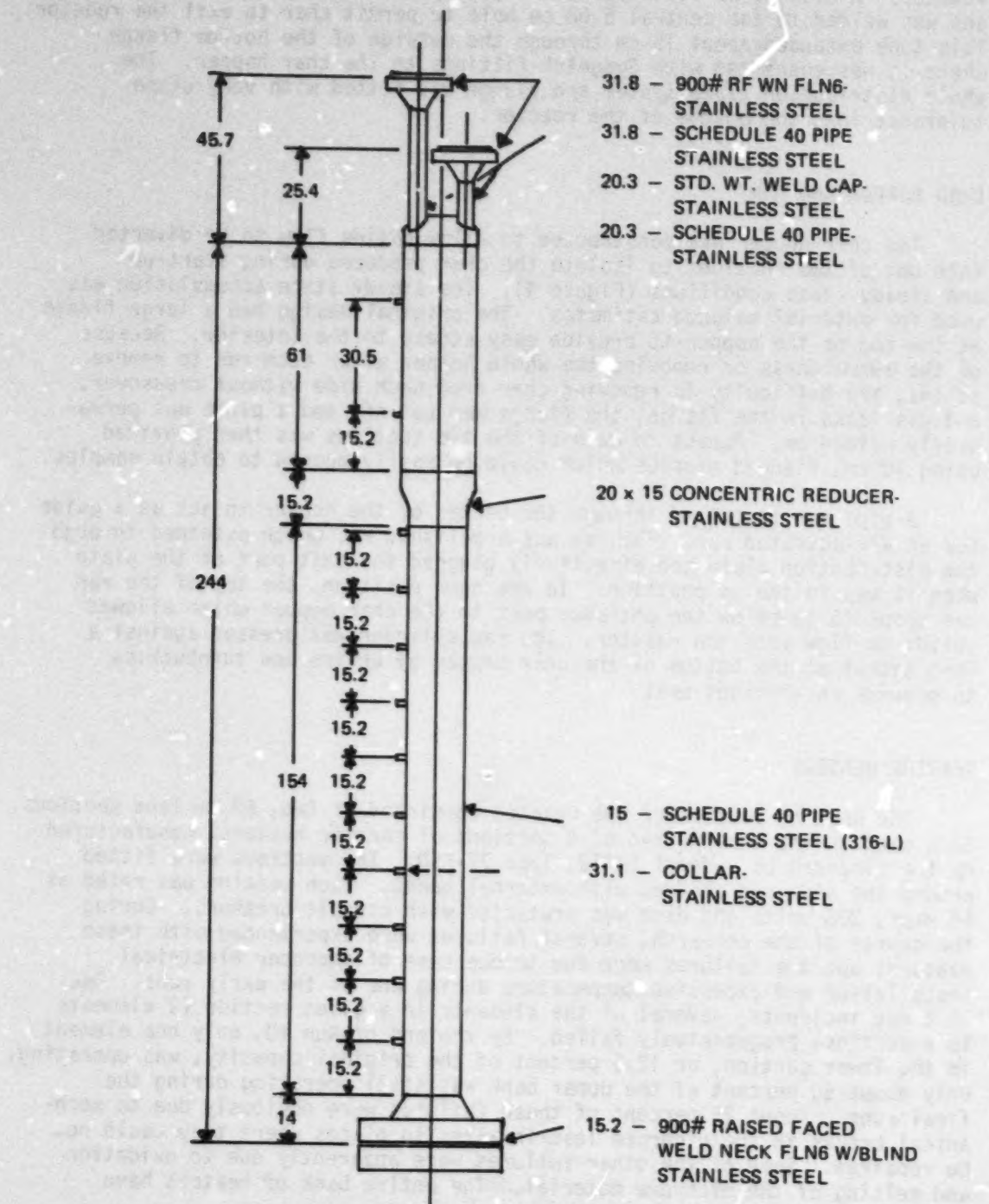


Figure 3. Reactor dimensions.

reactor. A 2.54 cm OD stainless steel tube passed through the bottom flange and was welded to the central 5.08 cm hole to permit char to exit the reactor. This tube extended about 15 cm through the outside of the bottom flange where it was connected with Swagelok fittings to the char hopper. The whole distribution plate system and flange was fitted with very close tolerance into the bottom of the reactor.

CHAR HOPPER AND RAM

The char hopper was constructed to allow solids flow to be diverted into one of two sections to isolate the char produced during start-up and steady state conditions (Figure 4). The steady state accumulation was used for material balance estimates. The original design had a large flange at the top of the hopper to provide easy access to the interior. Because of the awkwardness of removing the whole hopper after each run to remove solids, the difficulty in removing char from each side without crossover, and gas leaks in the flange, the flange was cut off and a plate was permanently welded on. Access to each of the two sections was then provided using 10 cm, flanged nipples which could be easily opened to obtain samples.

A pipe was installed through the center of the hopper to act as a guide for an air-actuated ram. The ram was a polished rod which extended through the distribution plate and effectively plugged the exit port of the plate when it was in the up position. In the down position, the top of the ram was about 15 cm below the entrance port to the char hopper which allowed solids to flow from the reactor. The ram cylinder was pressed against a lead gasket at the bottom of the char hopper by chains and turnbuckles to provide an airtight seal.

REACTOR HEATERS

The heating section of the reactor consisted of two, 60 cm long sections. Each section was constructed of 4 sections of ceramic heaters, manufactured by the Lindberg Co., Model 50752, type 77-KSD. The sections were fitted around the pipe and secured with external bands. Each section was rated at 40 amps, 206 volts and each was protected with circuit breakers. During the course of the research, several failures were experienced with these heaters, but the failures were due to one case of improper electrical installation and excessive temperature during one of the early runs. Due to these incidents, several of the elements in a given section (2 elements to a section) progressively failed. By the end of Run 10, only one element in the lower section, or 12.5 percent of the original capacity, was operating. Only about 50 percent of the upper bank was still operating during the final runs. About 25 percent of these failures were obviously due to mechanical breaks in the nichrome lead-in wires in places where they could not be repaired. Some of the other failures were apparently due to oxidation and melting of the nichrome material. The entire bank of heaters have been replaced.

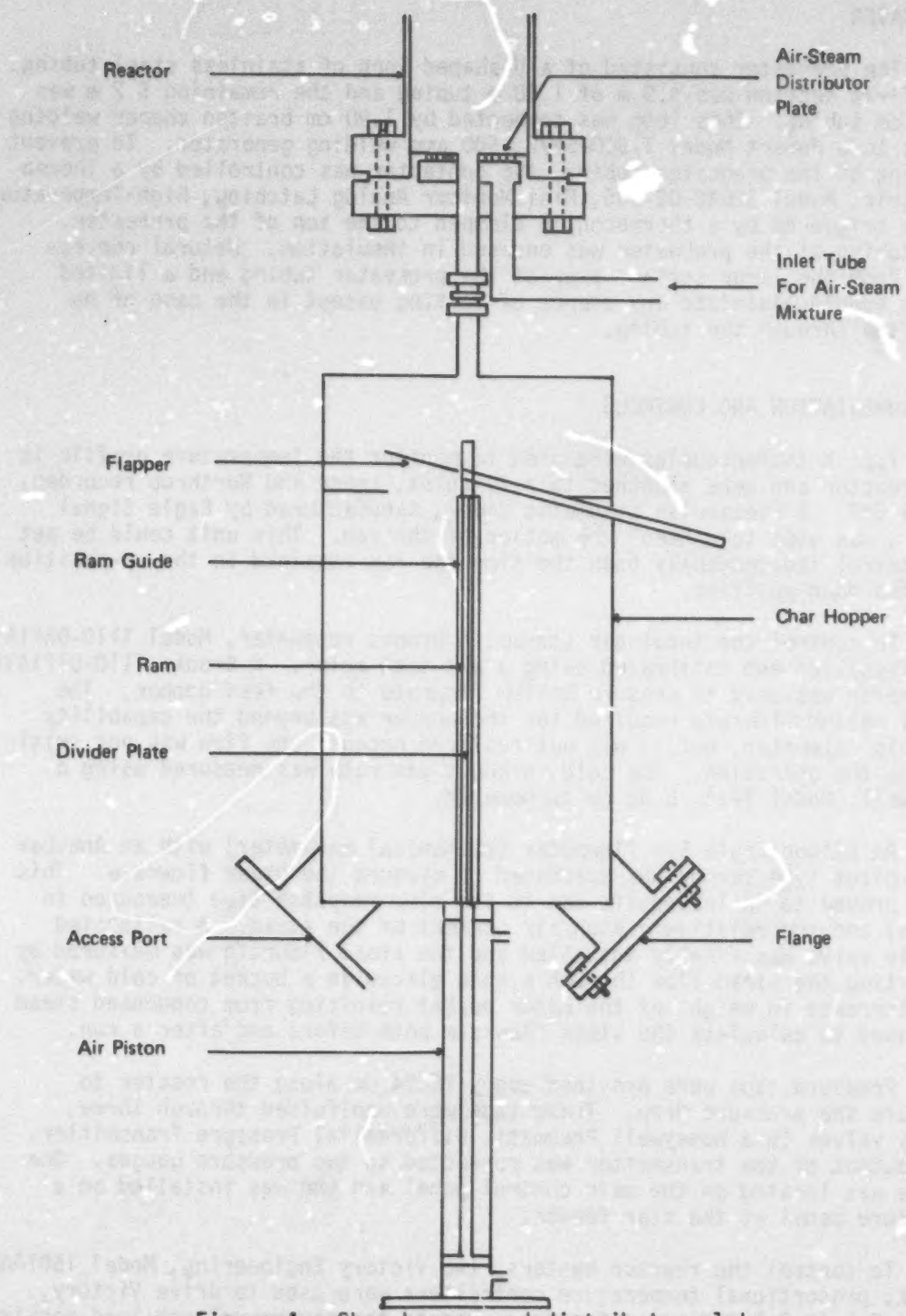


Figure 4. Char hopper and distributor plate.

PREHEATER

The preheater consisted of a U-shaped loop of stainless steel tubing. The first section was 4.9 m of 1.90 cm tubing and the remaining 5.2 m was 1.59 cm tubing. This loop was connected by 1.90 cm braided copper welding leads to a Hobart Model T-500-5422, 500 amp welding generator. To prevent melting of the preheater tubing, the contactor was controlled by a Thermo Electric, Model 32042-02-005, Mini-Monitor Analog Latching, High-Temperature Alarm triggered by a thermocouple clamped to the top of the preheater. The tubing of the preheater was encased in insulation. Natural convection from the large surface area of the preheater tubing and a limited power supply minimized any chance of melting except in the case of no air flow through the tubing.

INSTRUMENTATION AND CONTROLS

Type K thermocouples were used to monitor the temperature profile in the reactor and were attached to a 24-point, Leeds and Northrup recorder, Model 547. A Flexapulse pneumatic timer, manufactured by Eagle Signal Corp., was used to control the motion of the ram. This unit could be set in control independently both the time the ram remained in the up-position and the down-position.

To control the input air stream, a Brooks rotameter, Model 1110-06F1A1A, was installed and calibrated using a wet test meter. A Brooks 1110-01F1A1A rotameter was used to measure helium flowrate to the feed hopper. The final helium flowrate required for the hopper was beyond the capability of this rotameter, but it was not replaced because the flow was not critical to the operation. The cold, product gas rate was measured using a Rockwell, Model TP-4, 5.08 cm turbometer.

An Elison Eagle Eye flowmeter (mechanical manometer) with an Annubar semi-pitot type sensor was purchased to measure the steam flowrate. This unit proved to be inadequate due to its slow response time (measured in hours) and the relatively high air content of the steam. A calibrated needle valve was finally installed and the steam flowrate was measured by diverting the steam flow through a hose placed in a bucket of cold water. The increase in weight of the water bucket resulting from condensed steam was used to calculate the steam flowrate both before and after a run.

Pressure taps were provided every 15.24 cm along the reactor to measure the pressure drop. These taps were manifolded through three, 5-way valves to a Honeywell Pneumatic Differential Pressure Transmitter. The output of the transmitter was connected to two pressure gauges. One gauge was located on the main control panel and one was installed on a pressure panel at the star feeder.

To control the reactor heaters, two Victory Engineering, Model 1501AG-58-1K, proportional temperature controllers were used to drive Victory, Model Pak 10-0-1X triac contactors. Due to the severe voltage load required

for the controllers at startup and variable power supply, the original triac contactors were replaced and a capacitive bypass for surge protection was installed. New silicon-controlled rectifiers (SCR's), Vectrol, Model VSSC-1020-240-1FAC, were also installed which were capable of handling 63 amps at 240 volts with full surge protection. In addition, the original proportional controllers were modified using 2500 ohm variable center tap resistors on the output stages. The center tap was adjusted to provide voltage through a rectifying bridge to the 15 volt D.C. control circuit of the Vectrol SCR's (Figure 5).

A Fisher, Model 657-ES, pressure control valve with an integral Fisher Wizard, Model 4100ZR, controller was installed to regulate the pressure in the system. The pressure sensor for the control was located just after the reactor exit port in the 5.08 cm line leading to the cyclone

MODIFICATIONS

Although the reactor system operated successfully on the first run, extensive modifications were required to allow a wider range of operating conditions and to solve various problems that developed.

Feed Hopper

From the very first run, it was apparent that any steam entering the star feeder would cause the manure flow to stop almost immediately. Moist manure would be packed into a stiff paste by the mechanical action of the star feeder or would simply agglomerate to form a plug in the hopper above the star feeder. Initially, it was found that steam flow to the feeder could be prevented by the excessive use of helium flowrates (one cylinder per hour). A concentrated effort was undertaken to eliminate leaks. The ultimate solution required to minimize leaks required new, heavier seals on the 10 cm, feed inlet section at the top of the hopper and a new cone for the bottom of the hopper. It was also necessary to redrill the flange separating the cone and the hopper, reweld all the joints on the hopper, and install silicon seals on required flanges. These modifications cut the required helium flow by an order of magnitude.

Unfortunately, it was soon apparent that this was not enough. As the pressure rose in the reactor during startup, backflow (steam and gas) into the feed hopper occurred to equalize pressure in the hopper. If backflow occurred faster than adjustments to the helium purge flow rate, plugging resulted. To prevent this startup backflow from occurring, a 0.95 cm bypass line was installed between the top of the manure hopper and a point just below the star feeder. This line incorporated a 5 cm by 38 cm water-cooled condenser with a small reservoir and blowdown valve to condense any steam in the bypass stream.

To monitor any backflow that still inadvertently occurred, another Thermo Electric Mini-Monitor, Latching High-Temperature Alarm was installed with a warning buzzer. The alarm was actuated when the temperature below

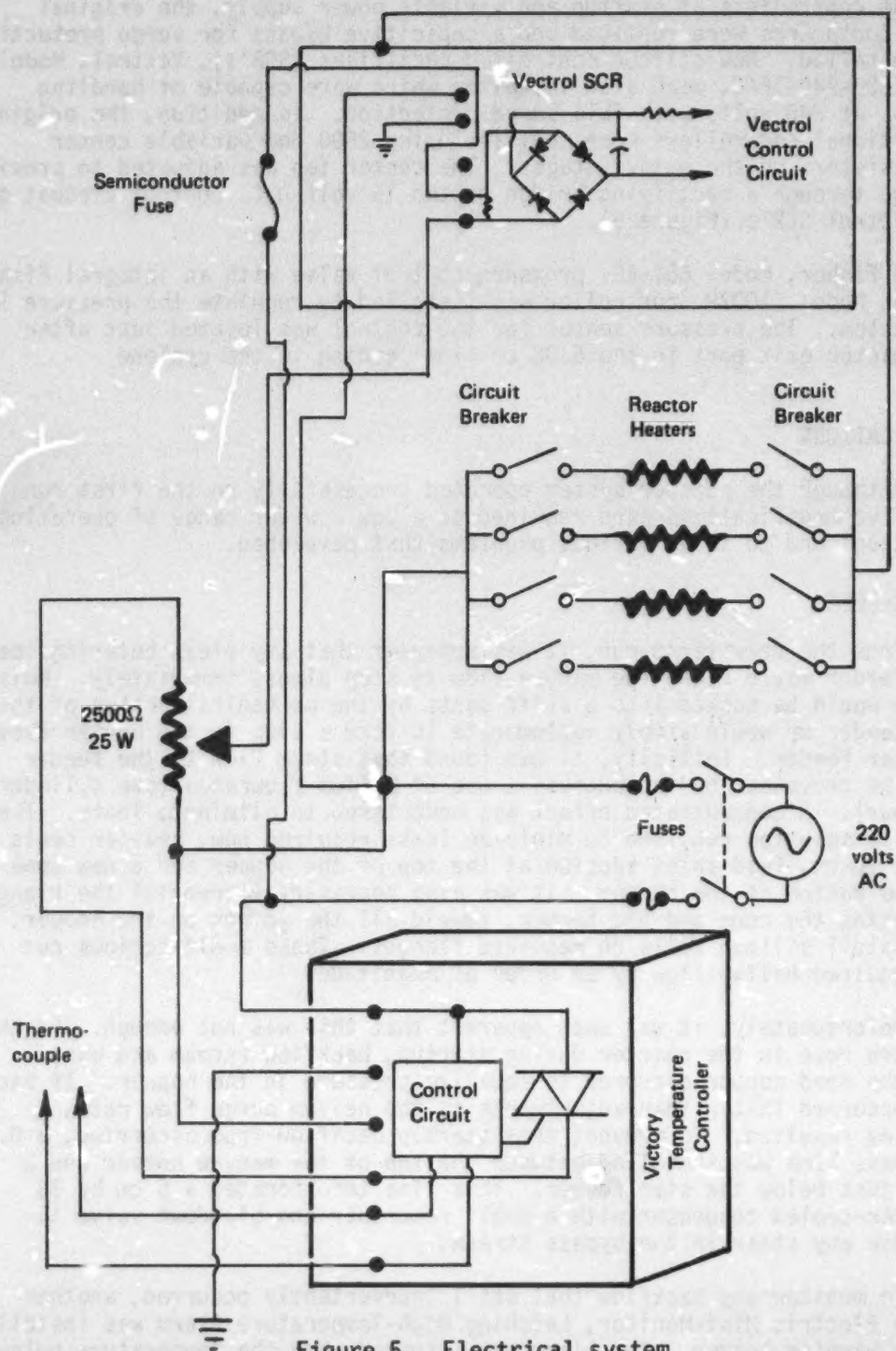


Figure 5. Electrical system.

the star feeder exceeded approximately 50°C. The alarm signal was used to set the helium flowrate after the startup was accomplished and this permitted more conservative helium flowrates to be used. All gas rate data have been corrected for the added helium rate.

Cyclone and Tar Trap

By the end of Run 4, it was apparent that the original filter arrangement for removing solids from the product gas was not acceptable. After a few runs, the filter became clogged with condensed tar and small particles. The clogging was apparently caused by the small surface area available, the dense packing of particles, the unheated design, and a high amount of solid entrainment (greater than expected).

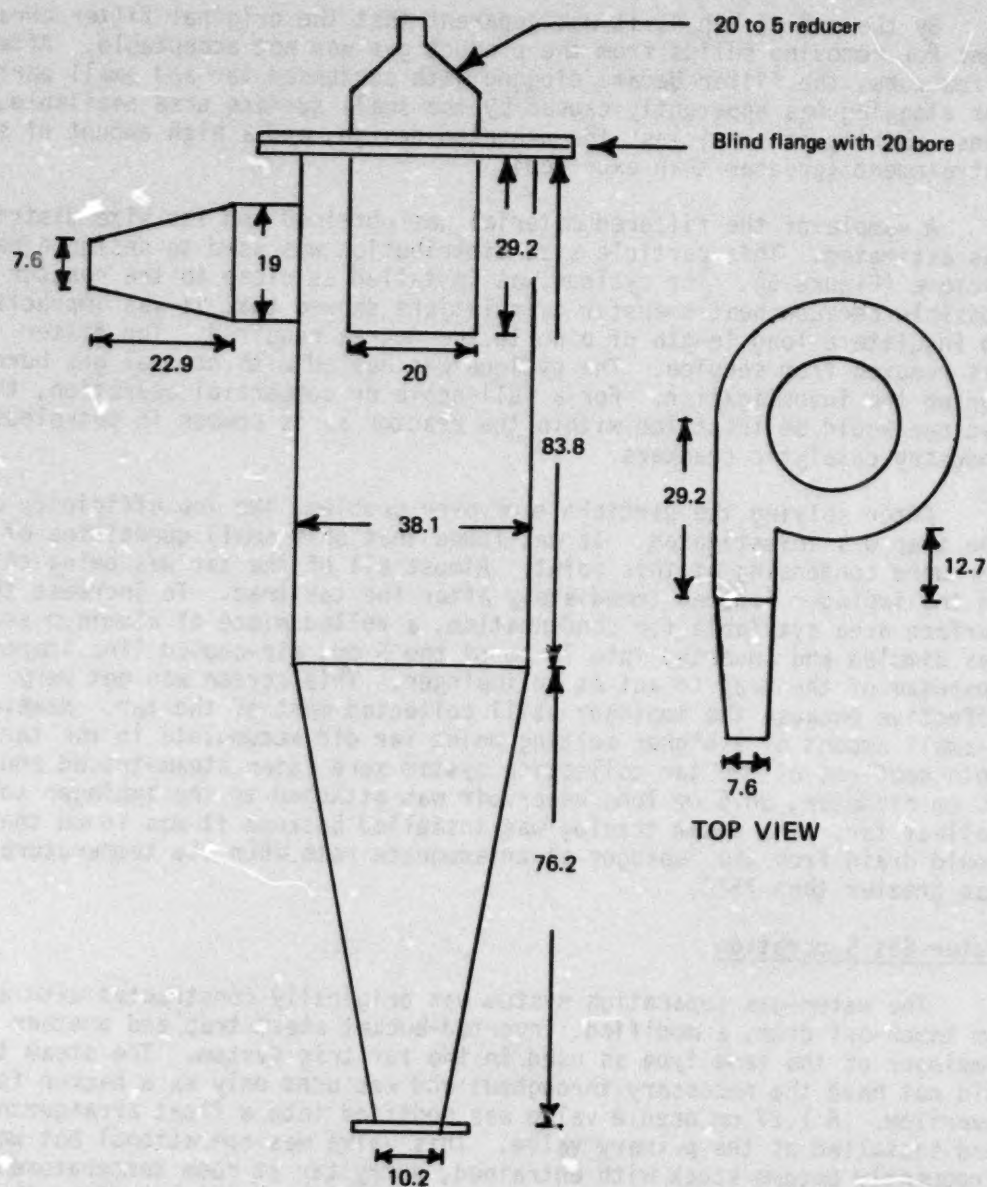
A sample of the filtered material was obtained and its size distribution was estimated. This particle size distribution was used to design a heated cyclone (Figure 6). The cyclone was installed as close to the reactor as possible because heat transfer calculations showed that it was impractical to insulate a long length of pipe to the degree required. The filter was removed from service. The cyclone was heated with natural gas burners during the investigation. For a full-scale or commercial operation, the cyclone would be installed within the reactor as is common in petroleum industry catalytic crackers.

After solving the particle carryover problem, the low efficiency of the trap was investigated. It was found that only small quantities of the tar were condensing at this point. Almost all of the tar was being collected in the impinger located immediately after the tar trap. To increase the surface area available for condensation, a rolled piece of aluminum screen was dimpled and inserted into 76 cm of the 5 cm, air-cooled line immediately upstream of the trap to act as an impinger. This screen was not very effective because the impinger still collected most of the tar. However, a small amount of a higher melting point tar did accumulate in the tar trap. Both sections of the tar collection system were later steam-traced and a 10 cm diameter, 30.5 cm long reservoir was attached to the impinger to collect tar. The steam tracing was installed because it was found that tar would drain from the impinger at an adequate rate when the temperature was greater than 75°C.

Water-Gas Separation

The water-gas separation system was originally constructed with a 5 cm knock-out drum, a modified, inverted-bucket steam trap and another impinger of the same type as used in the tar trap system. The steam trap did not have the necessary throughput and was used only as a backup for overflow. A 1.27 cm needle valve was modified into a float arrangement and installed as the primary valve. This valve was operational but would frequently become stuck with entrained, gummy tar at room temperature. Taps with a hammer were used to achieve a stable operation. After the last run of this investigation, a fire started in the tar trap due to an improper shutdown. This excessive heat vaporized or degraded the

(All Dimensions in Centimeters)



SIDE VIEW

TOP VIEW

Figure 6. Cyclone dimensions.

collected tars. These tars were carried over and plugged up the water-cooled condenser. Steam was used to clear the condenser, but further entrainment of the tars accumulated in the needle-valve, float assembly noted above. Rather than clean this assembly, a large, commercial float valve was installed.

Flow Measurement System

A very dilute mist of oil was entrained with product gas despite the cooling and condensation equipment that was installed. Some of this mist accumulated on the gas turbometer and would prevent rotation. To prevent fouling, another water-cooled condenser and a 3.18 cm diameter cyclone was added. A bypass of the turbometer was also installed because most tar was formed at startup. The small cyclone was observed to remove very little of the entrained liquid in the gas and a cloth filter was installed for final cleanup. The filter was effective, but the filter media had to be replaced every run because of internal by-passing and available surface area. A larger, final filter has been installed.

OPERATIONAL PROCEDURE

1. The reactor was heated to operating temperature using an approximate air purge rate of 5100 Standard Liter Per Hour (SLH).
2. After setting the helium purge rate, steam flow was initiated. The steam and air rates were then adjusted to those for a given run.
3. Once the system was thermally stabilized and the water removal system was functioning, the manure feed was started. A ram cycle of 3 seconds down and 10 seconds up was employed.
4. After the system reached a new thermal steady-state, the cyclone, tar trap and water containers were purged of accumulated material. The char hopper flapper was switched to the steady-state section and a run to collect gas, tar, and solids for a material balance was initiated. Gas samples for analysis were collected every 15-20 minutes.
5. The mass balance or run period was ended by switching the flapper in the char hopper back to the startup side. Gas, tar, water, and solid were then collected.
6. Gas samples were taken by connecting a gas sampling bottle across the sample loop and adjusting the pressure drop across the loop to 0.06 - 0.10 atmospheres.
7. The system was shut down by reversing steps 1, 2, and 3.

8. Char was removed from the hopper and weighed.

ANALYTICAL PROCEDURES

Gas samples were collected in 250 ml gas collection bottles and analyzed using a Varian Aerograph Gas Chromatograph with two columns. One column was a 3.65 m long by 3/16 in diameter tube packed with 50/80 mesh Poropak Q. A 1.2 m precolumn of 0.318 cm tubing packed with 50/80 Poropak R was used in conjunction with the Poropak Q column. These columns were used to quantitatively measure hydrogen, methane, carbon dioxide, ethylene, and ethane. A 3.65 m long by 0.318 cm diameter column packed with 45/60 mesh, 5 Å molecular sieve was used to measure hydrogen, oxygen, nitrogen, methane, and carbon monoxide. Runs 1 through 5 were analyzed through the courtesy of Young²⁹ who was studying the theoretical aspects of the pyrolysis process using a different chromatograph with similar columns.

A series of one ml volumes of air were injected before and after each samples series. The air peaks were averaged and a correction factor was estimated, which was used to adjust the sample peak heights. At least two separate injections on each column were made for each unknown sample. The peak heights were then converted to moles using calibration curves. Any oxygen present in the sample was estimated to be due to air contamination and was subtracted out along with a rationed amount of nitrogen.²⁹ The two columns were related by the amount of methane measured on each side. This procedure was refined, and a computer program was written to calculate the various run results from the chromatographs and other input data.

Sieve studies on the manure feedstock and char were done by shaking samples through standard sieves with an automatic sieve shaker for 10 minutes. The fractions were then weighed. Moisture content of the manure found by heating samples in a weighed crucible at 104°C overnight, desiccating, and then reweighing. Ash content was obtained by heating the sample in an air environment at 950°C overnight and then finding the weight differential. The bulk density of the solids was measured using a calibrated volumetric bottle. Because of the small total volume of the volumetric bottle, the sample density of large particles may be lower than the true value.

PREPARATION OF FEEDSTOCK

Manure was obtained from a local, commercial feedlot (Lubbock Feedlots). Based on the insensitivity of the process to the actual manure feedstock,^{24,29} the commercial manure pile was surveyed by visual examination and to find a reasonably dry, fresh manure for the feedstock. The commercial feedstock was collected and transported to the Texas Tech Feedlot where a standard, farm hammermill was used to grind the manure. A screen of 2.5 cm squares was used in the hammermill. The manure used in Runs 1 through

3 was sun-dried for a few hours on a large plastic sheet. The manure used for the remaining runs did not require drying. In Runs 1 through 8, the manure was only sieved to remove gross particles greater than about 1 cm in diameter. For Runs 9 and 10, the manure was sieved to eliminate particles greater than 1/3 cm in diameter.

SECTION VI

DISCUSSION OF RESULTS

OPERATION OF SYSTEM

A run was initiated by heating the reactor to the desired, nominal temperature and holding it at this level until the temperature of auxiliary equipment reached a steady level. This heat-up time was normally 4 to 7 hours during which an air purge of 5100 liters per hour (L/H) was passed through the reactor. Once a thermal steady-state had been achieved, a helium purge of the feed hopper was initiated to prevent steam from condensing in the inlet feedstock lines and starfeeder (Note: In a full-scale operation, a part of the product or waste gas could be diverted for this purpose; helium was chosen for this purpose because it was the carrier gas in the gas chromatograph). The desired steam and air flow rates for an actual run were then established and stabilized. After stable operation of the water-gas separation system was achieved, manure feed was introduced. The system was permitted to reach a new steady-state at the controlled reactor temperature. This new steady-state was generally achieved in 15 to 30 minutes. Gas, tar and char samples were then collected for analysis at 15 to 30 minute intervals. Reactor operation with manure feed ranged from 0.5 to 3 hours, excluding cooldown.

Only data from Runs 1, 6, 7, 8, 9, and 10 are discussed in this section because others were too short to provide reliable results. These short runs (2, 3, 4, and 5) were due to electrical heater failures and plugged, solids removal filters. This filter pluggage was the major reason for installing the cyclone shown in Figure 2.

EXPERIMENTAL RESULTS

The data from the operation of the large-scale reactor have been arranged and summarized in Table 1. A complete listing of results is given in Appendix 1. In general, these results indicated that dry gas yield and gas composition per unit of manure feed were largely independent of the air and steam feedrates, over the ranges studied. Reactor temperature was the only consistent variable which would order the data. This is in agreement with the results reported by Halligan, et.al. for a bench scale apparatus.^{24,25} These correlations and interpretations are discussed below, using an average reactor temperature calculated by the trapezoidal rule. The value given for the bench-scale unit was the arithmetic average of two measurements.

While it did not appear as a significant correlation parameter, oxygen in the air feed is a key reactor parameter because the partial oxidation of

Table 1. SUMMARY OF OPERATING CONDITIONS AND PRODUCT GAS DATA

Operating Conditions	Run Number									
	1	6a	6b	7	8	9	10			
Manure Feed Rate, kg daf/hr ^a	5.22	7.21	16.15	12.97	12.34	12.70	8.26			
Manure Feed Rate, kg ar/hr	7.76	10.60	23.61	18.96	18.05	18.01	11.75			
Air Feed Rate, kl/hr	1.149	1.700	1.487	1.904	1.402	4.249	0.765			
Steam Feed Rate, kg/hr	5.44	4.54	4.54	3.63	3.08	2.72	3.72			
Particle Size, in	<0.95	<0.95	<0.95	<0.95	<0.95	<0.32	<0.32			
Average Temperature, °C	711	695	641	617	629	668	628			
Product Gas Data ^b										
Total Dry Gas, l/g daf ^c	1.19	(0.667)	0.580	0.406	0.455	(0.718)	0.318			
Heat Value (HHV), cal/l	2855	2918	3790	3380	3523	2624	3345			
Gas Composition, vol %										
H ₂	25.2	22.2	20.0	28.2	17.4	15.1	20.9			
N ₂	14.6	27.8	15.1	23.2	26.7	36.8	24.2			
CH ₄	12.8	7.7	12.6	9.2	14.1	8.9	11.7			
CO	11.6	15.3	21.3	16.4	21.2	20.3	22.4			
CO ₂	30.8	20.7	22.1	15.4	14.1	14.2	14.8			
C ₂ H ₄	4.7	6.4	8.5	4.9	5.8	4.2	5.5			
C ₂ H ₆	0.3	0.5	0.4	2.7	0.7	0.5	0.5			

^a daf - dry, ash-free; ar = as received^b All data are average values from at least two samples. Individual gas samples were analyzed on the gas chromatograph using at least two injections.^c Values in parentheses are back-calculated values using a nitrogen balance.

the manure supplies part of the energy necessary to heat the manure feed-stock to reaction temperature. This exothermic reaction is indicated by comparing the average temperature of Runs 8 and 9 of Table 1. Run 9 was operated with three times the air flow of Run 8 with the same electric heat input. The apparent oxidation is indicated by a 39°C higher average reactor temperature. The significance of this temperature increase is indicated by noting that the total range of average temperature in Table 1 is 93°C.

CORRELATION OF DATA

The yields of total gas, ultimate hydrogen ($H_2 + CO$; see discussion below) and ethylene are given in Tables 1 and 2 and presented as a function of average temperature in Figures 7, 8 and 9, respectively (the correlation line through each data set is a least-squares fit). Comparison data from the bench-scale experiments of Halligan, et.al.^{24,25} are also shown in these plots. Because the slopes of these 3 data sets agree well with the bench-scale data, the general interpretation is that reactor temperature must be considered a key scale-up variable for the partial oxidation of manure as developed in these studies.

A preliminary analysis of the operating characteristics of the reactor has shown, however, that another parameter, volume fraction of solids, may be important because this parameter could affect heat transfer as well as alter the reaction history of particles. Such a factor may account for part of the scatter in the data, but sufficient detail has not yet been developed to identify the influence of this effect. A preliminary analysis on the effects of the volume fraction of solids on reactor operation is given as Appendix 2 of this report.

The apparent absence of oxygen or combustion effects on the product gas rate or composition may be explained in part by the high temperature of the reaction and the relatively low rate of oxygen feed. At the temperatures in the reactor, complete reaction of oxygen within 60 cm of the air inlet may be expected because the rate of feed is much less than stoichiometric. Confirmation of this is indicated by a detailed comparison of runs 8 and 9 discussed above.* In addition, the volume of combustion products is small because calculations have shown that combustion products only contribute 15-40% of the CO and CO_2 composition. The combustion or oxygen effect is also confused with electric heater input energy. Either of these two sources of energy can dominate, but the correlation variable is still temperature in terms of manure pyrolysis.

PRODUCTION OF AMMONIA SYNTHESIS GAS

Figure 8 and Table 2 illustrate the potential for the production of an ammonia synthesis gas from manure. As discussed by Halligan, et.al.,^{24,25}

Table 2. CALCULATED GAS PRODUCT DATA

	Run Number					
	1	6a	6b	7	8	9
Ultimate H_2 ($H_2 + CO$), 1/g daf	0.44	0.25	0.24	0.18	0.17	0.25
Ultimate H_2 : (N_2) Ratio	2.5	1.3	2.7	1.9	1.4	0.95
(Reformed H_2): (N_2) Ratio	8.0	3.8	9.5	4.7	4.9	2.6
(Reformed H_2 without C_2 's): N_2 Ratio	6.0	2.5	6.1	3.5	3.6	1.9
Ethylene Yield, 1/g daf	0.056	0.042	0.047	0.020	0.026	0.030
% C_2H_4 without combustion products	6.8	11.0	10.3	8.7	9.9	9.5
						8.7

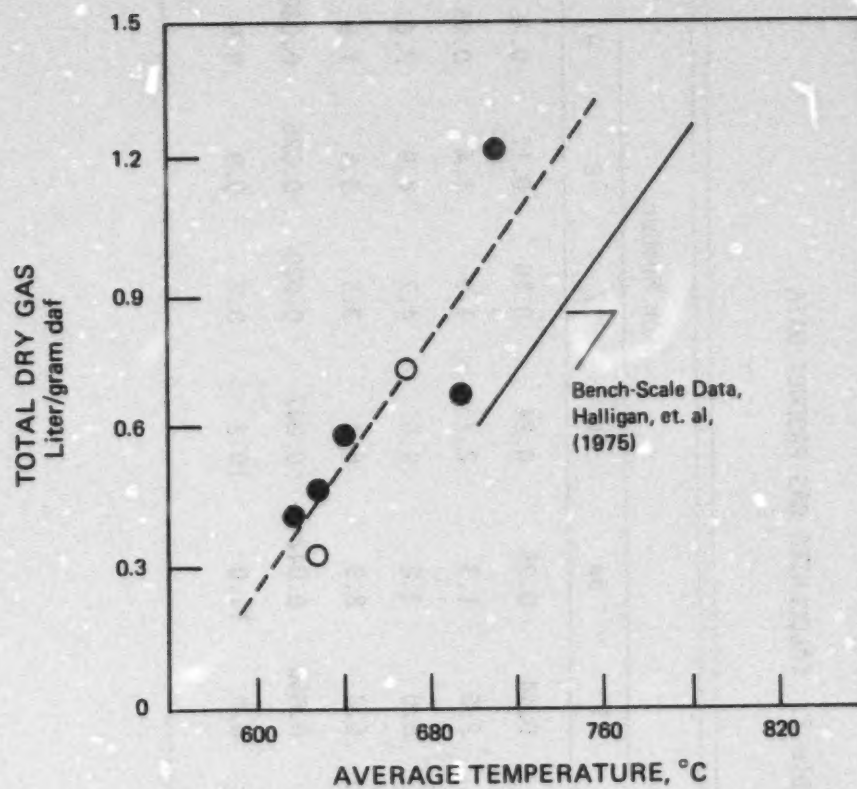


Figure 7. Influence of reactor temperature on dry gas yield.

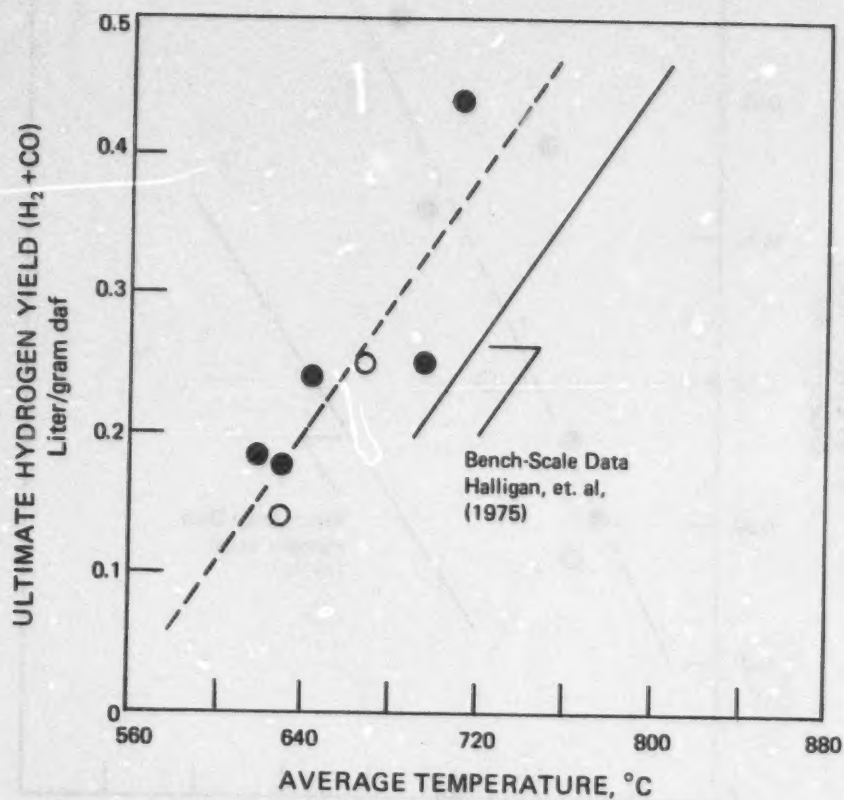


Figure 8. Ultimate hydrogen yield as a function of average reactor temperatures.

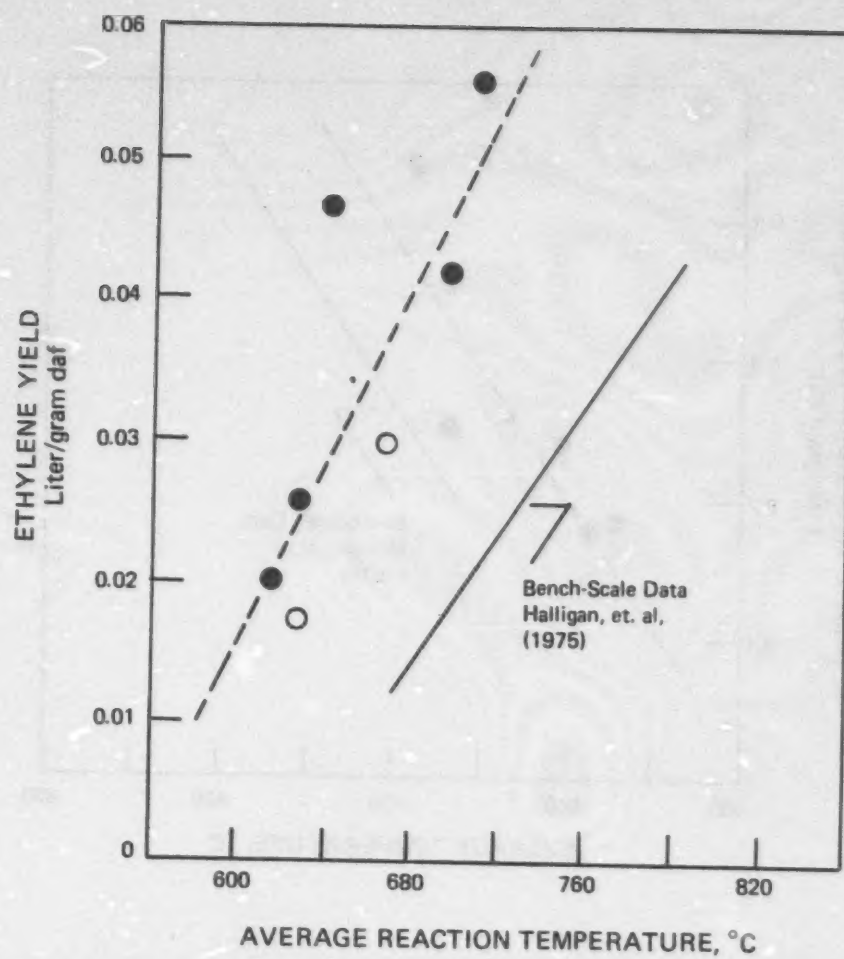


Figure 9. Ethylene yield as a function of average reactor temperature.

ultimate hydrogen is defined as the sum of $H_2 + CO$, assuming the CO is shifted as now accomplished in commercial ammonia plants ($CO + H_2O = CO_2 + H_2$). Reformed hydrogen is defined as the ultimate hydrogen plus the hydrogen that would result from the complete steam reforming of CH_4 and other hydrocarbons (e.g., $C_2H_4 + 2H_2O = 2CO + 4H_2$): the steam reforming step is also accomplished commercially using methane as a feedstock. These results (Table 2) show that the necessary molar ratio of 3:1 can be realized from the partial oxidation of manure over the range of conditions explored. It is recognized that the proper $H_2:N_2$ ratio can always be achieved by simply adjusting air feed at an imposed temperature. The objective of the reactor process is to achieve maximum air input to minimize external heat duty with the constraint of a $3H_2:N_2$ ratio. Another objective of ammonia synthesis gas production is to exploit the N_2 content of air, as opposed to viewing it as a diluent which must be balanced against the cost of manufacturing oxygen. Conversely, effective utilization of N_2 in the air from the process minimizes carbon; but, nitrogen utilization in agricultural sectors is of equal importance, if not more so, than carbon utilization which is a common goal of many coal conversion processes.

The results on ammonia synthesis gas production verify the small-scale reactor data reported by Halligan, et.al.²⁴ and the reader is referred to this reference for a more thorough discussion on the use and processing of this product. It is obvious from the data in Table 1 and Table 2 that the production of ammonia synthesis gas has not been optimized and that additional studies remain to be completed to develop the optimum. However, the data from both the large and small reactors do show that ammonia synthesis gas can be produced from cattle feedlot manure.

PRODUCTION OF ETHYLENE

The ethylene yield of Figure 9 illustrates one possible key difference between the large-scale and bench-scale reactors. As noted earlier, the large-scale reactor operates with a nearly complete countercurrent flow of solid and gas, with 5-20 percent of the total product char (as fine particles) exiting with the gas. This flow pattern was not achieved in the bench reactor and 67-87 percent of the solid char product was entrained. The higher fraction of hot, entrained solids (heat capacity about twice that of the gas) plus a review of the bench-scale operation indicates that product gas from the smaller reactor probably remained at temperature for a longer period of time. Thus, a higher degree of olefin cracking or pyrolysis would be expected for the bench-scale unit. This interpretation is supported by a $40^\circ C$ temperature shift in ethylene data (Figure 9) compared to a $20^\circ C$ shift in the total gas (Figure 7) and ultimate H_2 (Figure 8). The total gas or ultimate hydrogen rates would not be affected much ($< 10\%$) for a 3-4 percent change in ethylene composition. The net ethylene production would be a strong function of time and temperature because the rate of the three-halves, decomposition kinetics at 6 percent (vol) concentration and $600^\circ C$ is only 5.5 percent the rate of decomposition at $700^\circ C$. Alternately, the half-life at $600^\circ C$ is 1746 sec (6 percent vol) whereas it is only 67.7 sec at $700^\circ C$ using the data of Kunugi, et. al.³⁰

The production of ethylene (hence its time-temperature history) is of significant practical interest because the current sales value is 10-12 cents per pound and one major manufacturer indicates that a 20 cent per pound price may evolve by the early 1980's.³¹ Using a value of 0.05 L/g daf manure and the above current price, the ethylene in the synthesis gas has a sales value of \$11-\$14 per metric ton daf manure. The current data show that up to 70 kg C₂H₄/metric ton daf manure (approximately 0.56 L/g daf in Figure 9) can be produced; our studies indicate that reinjection of tars and oils produced in the reactor (10-30 percent by weight of manure feed) could potentially raise the ethylene yield to 80-90 kg/ton daf. Because the economics of ethylene production are attractive, it is important to note that several of the runs in Table 2 suggest that significant quantities of both ethylene and an ammonia synthesis gas could be produced at the same reaction conditions. Our current research goals are to collaborate the reported results and maximize the production rate of both an ammonia synthesis gas and ethylene.

EFFECT OF REACTOR OPERATION ON ETHYLENE PRODUCTION

During run one, 4.7 percent of ethylene was noted in the produced gas stream. This high concentration at a high maximum temperature (920-930°C) was attributed to a "quenching" effect in the upper half of the reactor, which had been established by the lack of adequate insulation. It was decided not to add additional insulation and investigate the possibility of increasing the production of ethylene because this olefin has a high sales value.

As a result of the light insulation, tremendous heat losses were sustained which made it difficult to achieve an accurate heat balance on the system and to develop critical interpretations on the reactor operation. However, detailed reviews of the temperature profiles of the hot reactor before adding manure and during operation provided some insight into the actual operating characteristics. These temperature profiles indicated that most of the combustion was occurring just above the distribution plate, perhaps confined to a height not more than 30 cm from the plate. This can be shown by comparing the temperature profiles of Run 8 and 9 as shown in Figure 10. In these two runs, only one heating element was operational and was at maximum capacity at all times. Run 9 had an air feed ratio about 3 times that of Run 8. All other feed rates were the same. The rapid temperature rise in Run 9 could only be accounted for by the release of heat through combustion. The possibility that a true fluidized bed could exist and distribute the heat within the lower section was judged to be unlikely because of the noticeable dip in the temperature profiles between the heaters where the reactor was very poorly insulated. The differences in the temperature profiles above the heaters could be due to a higher heat transfer coefficient inside the reactor in Run 9 at the higher total gas flowrate. The temperature difference beyond the heaters is, however, estimated to be of small importance compared to the differences in the lower part of the reactor.

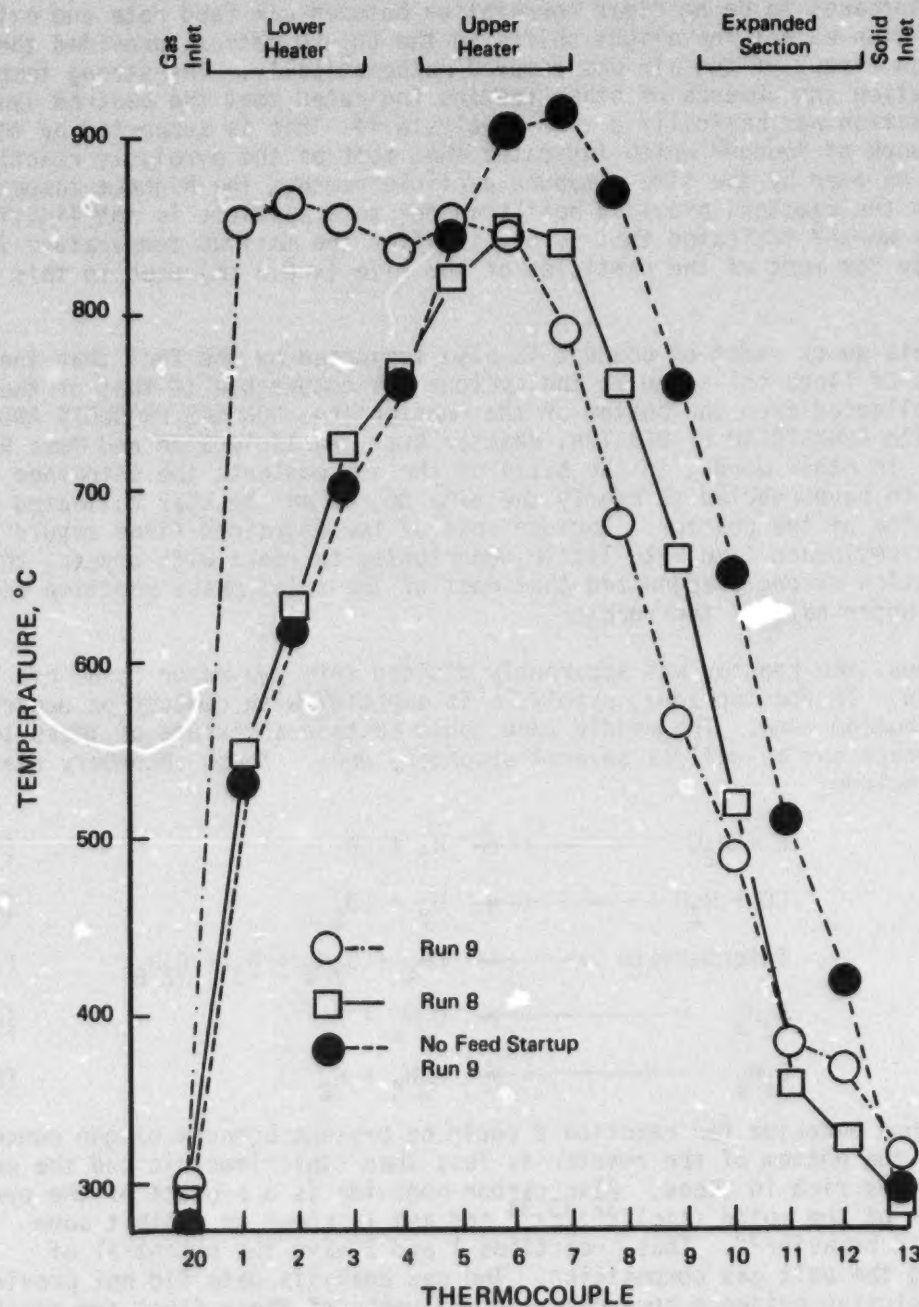
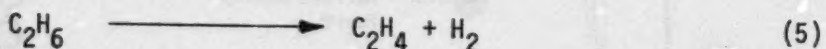
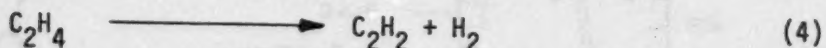
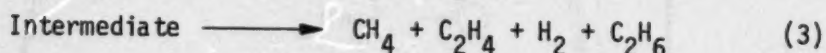
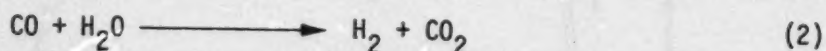
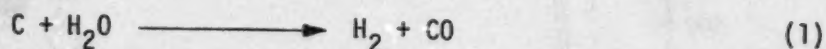


Figure 10. Temperature profiles in reactor.

As noted previously, temperature was the only correlating variable and there appeared to be no clear correlation between air feed rate and exit gas composition except for slight shifts in the CO₂-CO ratios, provided the dilution effect of the air was removed mathematically. The strong temperature correlation and absence of other factors indicated that the desired synthesis gas reaction was basically a true pyrolysis.⁴⁸ This is supported by the basic work of Young²⁹ which indicates that most of the pyrolysis reaction should be over by the time a manure particle reaches the highest temperature zone in the reactor, provided heat transfer to a particle is not limiting. Young's work²⁹ indicated that pyrolysis after the maximum temperature is unlikely for most of the particles of the size (< 0.3 cm) used in this study.

This quick reaction concept is also supported by the fact that the ash content of fines collected in the cyclone was comparable to that of the char collected from the bottom of the reactor (see NON-GAS PRODUCTS AND OPERATION DOWNSTREAM OF REACTOR, Reactor Char, Particle Size and Mass Reduction). In other words, on the basis of the ash content, the entrained fines appear to have reacted to nearly the same degree as the char collected from the bottom of the reactor. Because most of the entrained fines should have a lower residence time with little opportunity to react with oxygen, this observation strongly suggested that most of the solid-phase reaction occurs in the upper half of the reactor.

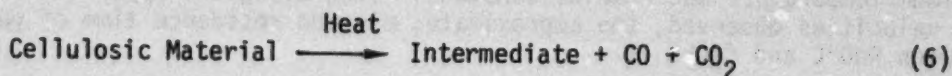
Thus, the reactor was apparently divided into two major zones of reaction. In the top zone, pyrolysis is expected with combustion occurring in the bottom zone. The middle zone could sustain a mixture of these two major reactions as well as several secondary ones. These secondary reactions might include:



The carbon monoxide for reaction 2 could be present because oxygen concentration in the bottom of the reactor is less than stoichiometric and the gas influent is rich in steam. Also carbon monoxide is a product of the pyrolysis reaction of the solid itself^{32,33,34} and ash is known to exhibit some catalytic behavior³⁵. Thus, reactions 1 and 2 have the potential of shifting the exit gas composition. The gas analysis data did not provide any conclusive evidence regarding the influence of these first two reactions. One would expect hydrogen concentration to be dependent upon these reactions and hence steam feed rate; but, hydrogen concentration did not correlate with steam feed rate. Again, temperature was the dominant factor. As also

discussed by Halligan, et.al.,^{24,25} the steam-carbon and steam-hydrocarbon reactions are estimated to have a minor role at the reaction conditions based on the results of other investigations. In particular, the rate of steam reactions are thought to be low because reactor pressure is 2 atm or less and average reactor temperature is generally less than 927°C (1700°F; 36, 37). Briefly, steam was added in the bench-scale experiments of Halligan et.al.^{24,25} as a "fluidizing" medium which could be easily separated from the gas products by condensation and a similar inert role was assumed for the larger unit. For example, without the addition of steam, the gas velocities in the larger unit would range from approximately 3 cm/sec. to 40 cm/sec instead of the actual 23-97 cm/sec.

In terms of the production of ethylene, the chemistry suggested that reactions (3), (4), and (5) above are probably the critical factors. Most reported results^{32,34,35} suggest that reaction (3) is preceded by reaction (6)



where the intermediate has been found to be largely composed of levoglucosan when the initial feed is pure cellulose and wood^{32,34}; a very diverse mixture with no major components is obtained when the cellulosic material contains high amounts of ash and other inerts.³⁴ It is crucial to note, however, that the final gas products and their relative amounts are not significantly affected, regardless of the actual type of cellulosic feedstock, as long as the same amount of total gas is produced²⁹. Thus, ash and inerts, roughly speaking, may catalyze to the degree of decomposition of the initial intermediate without significantly altering the desired, final step (the mixture of gas products).

Accordingly, the rate of decomposition of gases or the secondary pyrolysis reactions thereof appear to be the crucial factors in generating C₂ and higher hydrocarbons. A low rate of decomposition of C₂H₄ is desired and this appears to have been achieved in the SGFM reactor with a simple, practical design. It is known that ethylene can be produced from coal³⁸ and cellulosic³² feedstocks at significant concentrations (> 5%), but a sophisticated or high-vacuum apparatus has been generally required. Only one other practical reactor design has been reported to achieve such concentrations to our knowledge and that is the process developed by Garrett Research and Development for a sub-bituminous coal.³⁹ Most other processes have attempted only to maximize CO and H₂ to provide the usual, versatile synthesis gas. The SGFM process and the Garrett research offer a potentially significant advance in the state-of-the-art because the results suggest that valuable organics can be directly produced. Processes which produce only CO and H₂ obviously require additional reactors in order to provide organics. A detailed analysis of the production of ethylene in the SGFM reaction is presented below.

Based on the temperature profiles given in Figure 10 and the half-life data of ethylene given in the previous section, one may then estimate,

roughly, that the residence time of ethylene at temperatures greater than 800°C is on the order of 10 seconds or less, e.g., the half-life at 800°C is 9.0 seconds at a 6 percent concentration. This estimate of residence time does not, however, give a complete picture.

The maximum reported gas phase concentration of ethylene from a cellulosic feedstock or a derivative thereof is on the order of 20-25 percent^{32,40}. Allowances for dilution in the SGFM reactor indicate that the higher concentration may be 12 percent C₂H₄. When this value is combined with an isothermal, tubular reactor situation for the three-halves order reaction, calculations show that 6 percent ethylene is obtained in 6.38 seconds at 800°C. It is conceivable that the true half-life is much less because the decomposition of ethylene is still quite rapid down to 700°C.

To quantify the time-temperature history in the SGFM reactor more distinctly, assume that the maximum, total gas generation occurs at the maximum temperature and remains constant. Then using the upper limit of gas velocities observed, the approximate, minimum residence time of gas between 900°C and 600°C is

$$\text{velocity} = \frac{21234 \frac{1}{\text{hr}} \cdot 1000 \frac{\text{cm}^3}{1} \cdot 1 \frac{\text{hr}}{3600 \text{ sec}} \cdot 1 \frac{\text{atm}}{1.36 \text{ atm}} \cdot 1123^\circ \text{K} \cdot 4}{273^\circ \text{K} \cdot 3.14 \cdot 232 \frac{\text{cm}^2}{\text{cm}^2}}$$

$$= 76.9 \text{ cm/sec}$$

$$\text{residence time} = \frac{60.9 \text{ cm}}{97.9 \text{ cm/sec}} = 0.62 \text{ sec}$$

This residence time is of the same order of magnitude of the calculated half-life at 900°C at a concentration of 12 percent, 0.9 seconds. If the local concentration near a particle is assumed to be the critical factor, the ethylene concentration could approach 25 percent. For this case, the calculated half-life is 0.623 seconds at 900°C.

These estimates have been based upon idealized estimates. When combined with non-ideal features such as non-constant gas generation, backmixing of gas, potential catalytic surface effects and diffusion from a particle or droplet, then, these estimates on the time-temperature history of ethylene help explain why other processes (except for those of Garrett) have not yielded significant quantities of ethylene. The calculations also indicate that the important feature of the SGFM reactor design/operation may be the reasonably high velocity coupled with the parabolic temperature.

The previous estimates and discussion suggest the following physical description. Cold manure at room temperature enters the reactor and is heated by product gas to the initial reaction temperature of 250-300°C; initial decomposition of the solid then gives some CO and CO₂; further heating of the solid generates intermediates which decompose to hydrocarbon gases

(CH_4 , C_2H_4 , C_2H_6) and hydrogen. This valuable gas appears to be continuously produced as solid enters the high temperature zone and is immediately swept towards the feed section by the other generated gases, nitrogen, and steam. The continual sweep action into the low temperature environment minimizes further decomposition of the hydrocarbons to reduce the effective residence time below the value indicated above (0.6-0.9 seconds). The remainder of the solid then falls into the combustion part of the reactor to undergo further reaction to a char product (it is possible that heavy droplets of intermediate also enter this combustion zone).

The preceding calculations and description have been presented to illustrate the critical time-temperature history that may have been developed in the operation of the SGFM reactor. The calculations are, at best, only approximate because total gas velocities at all points of the reactor are unknown. The physical description must be considered preliminary. Nevertheless, these interpretations are thought to incorporate consistent reasoning for explaining the observed production of ethylene (see also section ETHYLENE FROM TAR/OIL PRODUCT) in the falling-bed, countercurrent design of the SGFM reactor. The ideal case is an infinite or near infinite temperature to achieve maximum manure pyrolysis to intermediates coupled with zero residence time to minimize hydrocarbon (CH_4 , C_2H_4) decomposition.

In summation, it is thought that the combination of the high countercurrent velocity (23-97 cm/sec) with the parabolic temperature profile (illustrated by Figure 10) has lead to the generation of the potentially valuable product gases. Neither the operating velocity nor temperature effects are novel in themselves nor do they appear to be particularly useful by themselves. It is the operating combination that may be important and permits: (a) a high conversion to be achieved to reduce the residue volume; (b) a high rate of total gas generation to provide valuable gas mixtures even with the dilution of nitrogen from air; and (c) a high yield of ethylene to maximize the potential product sales value. Obviously, additional studies are needed to confirm this hypothetical interpretation of the data.

A patent disclosure on the ethylene production was filed with the Environmental Protection Agency on July 17, 1975. A copy of this disclosure is given in Appendix 3.

SCALE-UP OF REACTOR DESIGN

The previous material has presented the results of the investigations which strongly suggest that ammonia synthesis gas and ethylene can be produced simultaneously from cattle feedlot manure using the SGFM reactor design and operation. This product mix indicates a promising process and one may legitimately ask "How can the reactor be scaled-up to a higher throughput, say, 200-500 tons per day for a demonstration plant?"

The question can be answered by the direct statement that the reported results do not provide a sufficient data base for a sound, engineering design or a reactor for the production of both products. To design a larger

reactor on the reported data would be an extreme extrapolation of the ethylene production technology. That is, the reactor was not originally designed to produce ethylene. The production of significant quantities of ethylene is a result of unanticipated operating conditions for a specific (or individual) reactor designed to produce ammonia synthesis gas. The data needed to specify residence time-temperature history in the SGFM reactor are currently unknown.

Design for Only Ammonia Synthesis Gas Production

The production of ammonia synthesis gas by itself appears to be relatively simple and direct without any evidence of subtle factors. This statement is based upon the results from the bench-scale reactor,^{24,25} the current pilot-scale reactor, and fundamental microreactor studies.²⁹ All of these studies show that reaction temperature is the only critical variable for the production of ammonia synthesis gas, providing feedstock particles are less than approximately 1.5 mm with approximately 80 percent being less than 1 mm (0.0394-inch or approximately 1/32-inch). The crucial design factors for the production of ammonia synthesis gas appear to be:

- Sufficient heat transfer to particles to assure that the entire volume of individual particles reach a temperature of 850-900°C; the time to heat particles to this temperature is sufficient for reaction.
- Sufficient fluid phase residence time to "crack" or decompose as much of the generated gases to hydrogen (H₂) and/or carbon monoxide (CO); again, the time required to heat the particles appears to be sufficient.
- Adequate amount of nitrogen (N₂) and oxygen (O₂) to achieve the desired 3H₂:N₂ ratio and an autothermal or near-autothermal operation.

These are the crucial factors and it is projected that the current results have demonstrated these factors to a degree that existing engineering technology for solid wastes^{39,41,42,43} and general petrochemical processing could be used to design and build a larger reactor. Some practical design information and improvements are still needed, but a larger, working reactor could probably be built and demonstrated after a reasonable shake-down or start-up period. This conclusion should, however, be verified by an independent engineering design review. The additional information required includes:

- Detailed data on the sulfur content of product gas to design a sulfur removal system.
- Reactor operation at 10-30 atmospheres to reduce compressor costs in supplying product to an ammonia synthesis plant. This should be accomplished in the larger plant with back-up on bench-scale unit because such operation exceeds our current capabilities; some high pressure investigations are planned in the near future.
- Detailed heat and material balance investigations to support the results obtained to date. This work is planned within the next

6 months and would be important in establishing a larger plant without overdesign.

- An analysis and treatment method for the waste water that is produced within the process.

Additional information that would be useful, but not necessary for design, should include data on alternate or mixed-manure feedstocks. These feedstocks could include other residual cellulose or biomass from the agricultural or forestry sector such as cotton burrs and gin trash; sawdust; field stubble; and corn and other stalks. It is important to note that while information on these new feedstocks is not necessary for the reactor design and scale up, the data may be needed to assure that a practical, full-scale plant can be economically justified. That is, the cattle feedlot industry is a highly volatile one and other cellulose may be needed to assure that feed to sustain a high volume operation (1000-2000 ton per day) is always available within a 30-50 mile radius of the plant site. The use of alternate or mixed feedstocks would also expand the realm of application to other agricultural locales besides high-volume feedlots and is highly recommended as a subject for further investigation.

Design for Ethylene and Ammonia Synthesis Gas Production

As noted, the information for the design of a reactor to produce ethylene along with synthesis gas is not available: the data that specify the existing ethylene residence time-temperature history. Part of these data should be obtained within the near future and will include information on the complete gas composition within the reactor. These internal, gas composition data will provide a direct knowledge of where the ethylene is formed. Analysis of the data will also help specify the ethylene decomposition rate by comparing the data to pure gas reaction rate data and velocity of the total gas stream along the reactor using a nitrogen balance. This information will be used to develop new operating conditions and techniques for improved ethylene production. The new techniques could include re-injecting the liquid tar product that is currently produced (see ETHYLENE FROM TAR/OIL PRODUCT, page 44). To establish a firm data base, studies should also investigate (1) the degree of solid and gas phase backmixing within the reactor; (2) the hold-up volume of solid in the reactor; and (3) the operation of a 2 or 3-stage set of true fluidized beds as opposed to the falling bed, countercurrent operation.

Action Taken on Needed Design Data

A program has been funded by the U. S. Energy Research and Development Administration to obtain detailed heat and balance data; internal gas composition data; and bench-scale data on several alternate feedstocks with scale-up of one. This new program began in September 1976.

MATERIAL AND HEAT BALANCES

The major effort over the past year was to develop a working reactor system. During the course of the investigation, several mechanical problems were encountered and solved; but, unfortunately, some of the problems destroyed any possible chance of obtaining a complete material balance on all runs. The best results are given below. The original equipment train was designed to provide a reliable heat balance; but, again, to develop a working system, much of the original design was modified (see EXPERIMENTAL EQUIPMENT, PROCEDURES, AND MATERIALS) which nullified any accuracy and precision within the available time frame. Some calibration for heat balances has been completed and the results are reported below.

Material Balance on Reactor and Gas Analysis

The two, most reliable material balance run data are given in Table 3. The results show that 11-14 percent of the total mass input or output was not measured at designated sample or collection junctions. There are several possibilities for this discrepancy. After reviewing all data, operating characteristics, and observing the tar build-up inside transfer lines, it was concluded that a significant part of this discrepancy was due to uncollected tar and solid fines in transfer lines, and, probably, solid hold-up in the reactor and cyclone. Because the reactor and cyclone were allowed to discharge solid 3-4 hours after stopping the manure feed, it is believed that a majority of the unaccounted mass is tar deposited on the inside of transfer lines. Preliminary estimates indicate that the tar product has a density somewhat greater than water. Thus, for 5.08 cm ID transfer lines, the estimated thickness over 914 cm of pipe for 1500 g of unaccounted material is:

$$\text{Tar Film} = \frac{\text{cm}^3}{1.04 \text{ g}} \times \frac{1500 \text{ g}}{914 \text{ cm} \times 3.14 \times 5.08 \text{ cm}} = 0.98 \text{ mm}$$

= approx. 1/32 in.

This coating thickness is well within the visual inspection of transfer line tubing and supports the projection that a significant fraction of tar was deposited on pipe walls. Further evidence of this observation is that a fire started in the main transfer line between the cyclone and tar trap during improper shutdown of Run 10 and was self-sustaining for several minutes before being extinguished.

Because the gas product is of major interest, it is important to note that nitrogen balances using measured gas flow and gas composition agreed within approximately 10 percent after the first fifteen minutes of operation with manure with a clean turbometer (Run 6) or after installation of the final filter prior to the turbometer (Run 10). Some of the individual measurements did, however, deviate by as much as 34 percent and for this reason, the average of the directly measured data was used in the correlations

Table 3. SELECTED MATERIAL BALANCE AND ASH DATA

Item	Run Number	
	8	9
A. Material Balance		
1. Input, kg		
Wet Manure (10% moisture)	18.05	12.94
Air	1.72	3.86
Steam	<u>3.06</u>	<u>9.95</u>
Total Input, kg	22.83	18.75
2. Output, kg		
Gas	5.74	7.08
H ₂ O + Organics	6.44	4.88
Tar	0.23	0.23
Solid Fines (Cyclone)	0.63	0.74
Char	<u>7.03</u>	<u>3.74</u>
Total Output, kg	20.07	16.67
% Output/Input	87.91	89.91
% Unaccounted Output	12.09	11.09
B. Ash Content, wt. %		
Manure Feed	21.54	19.59
Cyclone, Solid Fines	55.50	49.45
Char	50.24	46.50

discussed previously. Thus, the volume of total gas output does have some uncertainty and this does affect the material balance in Table 3. The gas rate uncertainty could be 0.5-1.0 kg in both of the data sets cited.

With regard to the reliability of gas composition analysis, it is important to note, as discussed in the section Analytical Procedures (page 20), that 2 or more readings were obtained per gas sample and each reading was the average of 2 or more injections. Also, the gas composition data of Run 1 were analyzed on a different chromatograph by a different operator and the calibration used for the reported gas composition was confirmed by different operators using the SGFM instrument after 6 months operation. An infrared scan from 400-4000 Kayzers (approximately 2.5-18 microns) on a sample of condensed gas (N_2 boiling point) from Run 1 showed that there were no major components in the gas other than those listed in Table 1 except for a small amount of C_2H_2 ($< 0.5\%$). Thus, in general, it was concluded that the reported gas composition is accurate; precision is not estimated to be better than 2 significant figures.

Heat Balance on Reactor

As noted earlier, it was not possible to obtain reliable heat balances during the runs due to extensive modifications. A recent calibration of the reactor using only an air input has shown that the heat loss from the reactor without feed is approximately 95 percent. This heat loss is largely due to the relatively poor insulation at the top of the reactor which is thought to provide the quenching effect noted earlier in discussing ethylene production. Other data and calculations show that the convective (natural) heat transfer coefficient from the reactor is 4-5 Btu/hr ft² °F, which is the expected range of values for natural convection from a vertical cylinder.

These results suggest that the reaction as operated is potentially near the desired autothermal case. Additional data are required before this can be ascertained.

NON-GAS PRODUCTS AND OPERATION DOWNSTREAM OF REACTOR

Reactor Gas and Cyclone Tar

The gas phase exiting the reactor contained 5-21 percent of the total collected char, by weight. This solid consisted of particles with diameters ranging from 250 μ m-20 μ m as removed in the cyclone with smaller sizes being entrained further downstream.

The appearance of the exit gas (before treatment) was that of a dense smoke with a greenish-yellow tinge and a very unpleasant odor, something approaching that of wet manure itself. This description of the gas is apparently the "standard" product because we soon learned to associate the odor with good operation, until most of the leaks were eliminated.

The gas also contains tar which apparently makes up the major fraction of the aerosol or smoke. This tar begins to condense at approximately 320°C

and this was the basis for operating with a heated cyclone. With the cyclone maintained at approximately 300°C, no significant condensation of the tar occurred and a free-flowing solid was discharged.

Tar and Condensation

As noted, tar began to condense at approximately 300°C and product was obtained down to room temperature. Most of the collected tar was obtained at 100-120°C but it would appear (Material Balance) that a significant fraction condenses above this temperature and that a new condenser is needed to collect all tar. One has been designed and constructed, but not tested.

The tar collected at different temperatures has a noticeably different appearance. The high temperature fraction tends to form a grainy, discrete deposit at room temperature; its viscosity is greater than molasses at 100°C. The initial visual observation suggests that this material is simply entrained fines from the cyclone with some condensed tar. However, the ash content of this fraction is less than 1 percent and the material is volatile.

The low temperature fraction (the fraction collected at 100-120°C has the consistency of taffy at room temperature. At the collection temperature, the fraction flows easily with a viscosity somewhere between water and molasses. The fraction has an odor which approximates that of crude oil, without hydrogen sulfide.

The tar impinger used to collect tar at 100-120°C worked very well and removed approximately one pound of tar per hour. This design could be used for a final tar collection in future reactors following collection units which condense the tars with apparent boiling points greater than 120°C.

Water Condenser and Product

The product stream from the water-cooled condenser was a brown to yellow, murky, foul-smelling liquid with a high sediment content. Over a period of several weeks, the liquid separated into three phases: a foamy (organic?) layer, a dark, watery layer, and a layer of sediment. This "waste" water could be a severe pollutant, but current projections are that the organics could be recovered by passing the stream through a bed of the char product (similar to an activated charcoal bed). The bed solid plus adsorbed matter could then be burned to produce steam or mixed with fresh manure feedstock to recover valuable carbon and hydrogen. A gradient-temperature condensation system below 100°C might permit a large fraction of the organic layer to be collected separately. Either of these alternatives would minimize the pollution potential. Further investigations on this procedure are needed to develop a complete process design.

In general, the operating problems caused by condensable products (tar, aqueous mixture, etc.) from manure pyrolysis must be experienced to be appreciated fully by any investigator. This conclusion has been confirmed by other investigators, and specifically during manure pyrolysis.⁴⁶

Reactor Char, Particle Size, and Mass Reduction

The main fraction of the produced char (80-95 percent) exited from the reactor as a free-flowing solid material with an approximate average particle size of 70 μm . The solid burns quite easily and, in some cases, the problem is how to keep the hot solid (200-300°C) from burning when exposed to the atmosphere. For example, hot char was once dumped into a bucket with a plastic bag. A low-level surface fire developed. Part of the solid was dumped on a cold steel plate in a 5-8 cm pile. This material, under controlled conditions, continued to burn for several hours, without a noticeable smoke or odor.

A supplemental, combustion test of the char was run in a two-stage, commercial furnace used to burn waste cotton.^{47,48} The brief test indicated that there were no problems except for the expected high ash fraction (50 percent).

The distinction between particle size of the various runs in Table 2 and Figures 7, 8, and 9 has been made because product char particles with effective diameters greater than 0.318 cm were visually observed to be grossly underreacted. A representative sample was sieved and the ash content of the various fractions was obtained to confirm the visual observation. These results (Table 4) indicate that approximately one-third or more of the original volatile mass remained for those particles greater than 2 mm (approximately 1/12-inch) compared to 15-20 percent for particles less than 1.5 mm. The calculation for these estimates in Table 4 is as follows:

A = mass of ash = constant

α = original ash fraction

V_o = original volatile mass

β = final ash fraction

V_F = final volatile mass

$$\frac{A}{V_o + A} = \alpha$$

$$\frac{A}{V_F + A} = \beta$$

$$\frac{V_o}{V_o + A} = 1 - \alpha$$

$$\frac{V_F}{V_F + A} = 1 - \beta$$

$$\frac{V_F}{V_o} \frac{V_o + A}{V_F + A} = \frac{V_F}{V_o} \frac{A}{\alpha} \frac{\beta}{A} = \frac{1 - \beta}{1 - \alpha}$$

$$\frac{V_F}{V_o} = \frac{\alpha(1 - \beta)}{\beta(1 - \alpha)}$$

Table 4. EFFECT OF PARTICLE SIZE ON ASH CONTENT

<u>Particle Size</u>	<u>% Ash</u>	<u>Approximate % Volatiles Remaining</u>
A. Feed	19.6-21.5	100
> 2 mm	-	-
1.41-2.0 mm	-	-
1.05-1.4 mm	-	-
0.71-1.05 mm	-	-
< 0.70 mm	-	-
B. Char Product ^(a)		
> 2 mm	41	36 ^(b)
1.41-2.0 mm	56	20
1.05-1.4 mm	55	20
0.71-1.05 mm	54	21
< 0.70 mm	59	17
Cyclone (< 0.70 mm)	60-61	16

^(a) Run 8

^(b) $100 \times V_F/V_O$; $\alpha = 0.20$ was used in these calculations

These results suggest that particles less than 1.5 mm (approximately 1/16-inch) will be volatilized to a reasonable degree (80 percent) and that excessive grinding of manure is not required for the SGFM process. The use of large particle sizes is actually desired to minimize carry-over. The apparent lack of effect of the 0.318 cm sieving noted in Table 1 is due to the fact that 80 percent of the particles as run are less than 1.5 mm.

These same results show that the reduction in total mass of the original solid waste is $= 100 - ((V_F + A) \div (V_O + A) \times (100)) = 100 - \alpha \div \beta \times 100 = 51 - 68$ percent. The average reduction is approximately 60 percent for Run 8 and a range of 55-65 percent was observed throughout the investigation. The results also show that 60-85 percent, with an average value of 80 percent of the volatile mass that can be treated has been accomplished. It is anticipated that the proposed process would use the char product for steam regeneration or other uses; hence, 100 percent of the volatile mass would be eliminated with only ash to be disposed. Mackenzie⁴⁶ and Sweazy⁴⁹ should be consulted for possible uses of the final ash product.

ETHYLENE FROM TAR/OIL PRODUCT

The tars from the SGFM process at 100-130°C have been subjected to oxygen-free, pyrolysis using a bench-scale reactor. This work was undertaken to determine the feasibility of reinjecting tar products into the large-scale SGFM reactor. This work is not yet complete, but the preliminary results (40) given below do indicate that reinjection may be advantageous.

Briefly, the bench-scale reactor for tar pyrolysis is a heated tube with a basket containing a tar sample. After a stable, specified temperature profile along the reactor is achieved, the basket with unreacted tar is lowered to a selected position which determines the reaction temperature of the tar and the residence time-temperature history of the evolved products. Helium is used as sweep gas at all times.

Reaction products consist of char residue, new tar products and gases. The new tar is separated from the gas product using 3 condensers in series. The gas is collected and held for analysis using a gas chromatograph.

The gas chromatograph used for the tar pyrolysis investigation is not the same unit used for the analysis of gas from the large-scale SGFM reactor. These two chromatographs have been calibrated by different individuals and are run at different temperatures to suit particular study needs. Thus, it is significant that the two analyses agree on the gas composition of a given unknown tar pyrolysis sample, within ± 9 percent relative error for 5 components out of 7 with compositions greater than 2 percent. For the 2 other components which are present at concentrations less than 2 percent, the error increases to 25-30 percent.

The preliminary results from the tar pyrolysis investigation are given in Table 5. The cited range of values are from 12 runs at various tar and

Table 5. PRELIMINARY RESULTS FROM TAR PYROLYSIS

Maximum Reaction ^a Temperature °C	Products Obtained, % of Sample Fed			
	Total Gas	Residue	Ethylene	Methane
700	9.2-14.8	52.7-63.9	1.5-3.3	0.9-1.6
800	18.4-24.7	40.8-56.9	4.4-7.13	1.8-2.9
900	27.2-33.2	33.4-46.3	7.6-10.6	3.2-4.8

^aThis temperature is thought to be indicative of the operation of the large-scale SGFM reactor.^{13,29}

gas residence times. Individual runs have been duplicated within ± 7 percent relative error for the results cited. These initial data show that tar reinjection may be very attractive because ethylene yield from the tar at 900°C is comparable to that for manure itself, 0/075-0.106g/g of daf feed. The data also show that similar levels of total tar conversion may be obtained or approximately 50-65 percent. The ethylene concentration in the gas phase itself is in the neighborhood of 25 percent molar and significant concentrations (3-5 percent) of another valuable olefin, propylene, have also been observed. Current correlations among the data indicate that the tar pyrolysis/reinjection is compatible with the large-scale SGFM reactor, i.e., maximize operating temperature (see Table 5 where conversion at 900°C > 600°C > 700°C).

In addition to the practical implications of these preliminary data, the results also strongly suggest that manure pyrolysis actually proceeds through a low molecular weight intermediate (tar) step which is in agreement with basic studies on pure cellulose, wood, and municipal solid waste^{29,32,34,35,50,51,52}. The results which support (not confirm) this mechanism are (a) ethylene yield is comparable to manure based yield¹³; (b) product gases are similar to solid pyrolysis data, including CO and CO₂^{29,32,35}; and (c) maximum reaction temperature is comparable to that for solid manure samples at comparable residence times for similar conversion levels^{13,50,51,52}. However, the production of combined propylene and butenes (5-10 percent in gas phase) exceeds that previously measured in basic solid pyrolysis studies or from the large-scale reactor. These compounds will decompose at reaction temperature if the residence time is long enough. Thus, their absence in the gas from the large-scale SGFM suggests the importance of gas phase, time-temperature history or possibly the importance of decomposition within a solid particle. Thus, one may project that further optimization of time-time-temperature history in the large-scale reactor would be required to recover, say, propylene.

Most of the work on the tar pyrolysis project is directed to estimating the effects of tar and gas phase residence time on gas yield and composition. The results will be used to estimate the point(s) of tar injection in the large-scale SGFM reactor and as supporting data in developing a consistent model of the manure reactor kinetics.

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APPENDIX A

TABLE A-1
OPERATING CONDITIONS FOR INDIVIDUAL RUNS AND SAMPLES

OPERATING CONDITIONS		RUN AND GAS SAMPLE NUMBER									
Manure Feed Rate, As Received		1-4	1-5	6a-1	6a-2	6a-3	6b-6	6b-7	7-2	7-3	8-3
kg/hr		7.76	7.76	10.6	10.6	10.6	23.6	23.6	19.0	19.0	18.1
lb/hr		17.1	17.1	23.3	23.3	23.3	52.0	52.0	41.8	41.8	39.8
Manure Feed Rate, Dry-Ash Free											
kg/hr		5.22	5.22	7.22	7.22	7.22	16.2	16.2	13.0	13.0	12.4
lb/hr		11.5	11.5	15.9	15.9	15.9	35.6	35.6	28.6	28.6	27.2
Air Feed Rate											
k1/hr		1.15	1.15	1.70	1.70	1.70	1.49	1.49	1.90	1.90	1.40
SCF/hr		40.5	40.5	60	60	60	52.5	52.5	67.2	67.2	49.5
Steam Feed Rate											
kg/hr		5.45	5.45	4.54	4.54	4.54	4.54	4.54	3.63	3.63	3.09
lb/hr		12	12	10	10	10	10	10	8	8	6.8
Particle Size, less than											
cm		0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95
inch		3/8	3/8	3/8	3/8	3/8	3/8	3/8	3/8	3/8	3/8
Raw Gas Production Rate											
1/g daf		1.19	1.19	0.693	0.645	0.562	0.544	0.613	0.480	0.327	0.467
SCF/lb daf		19.1	19.1	(11.1)	(10.4)	(9.0)	8.71	9.83	7.69	5.24	7.49
Run Time With Manure, hr											
		0.6		1.13			1.0		1.6		2.3

TABLE A-1 (continued)

OPERATING CONDITIONS		RUN AND GAS SAMPLE NUMBER									
Manure Feed Rate, As Received		8-4	8-5	9-1	9-2	9-3	9-4	10-1	10-2	10-3	10-4
	kg/hr	18.1	18.1	18.0	18.0	18.0	18.0	11.8	11.8	11.8	11.8
	lb/hr	39.8	39.8	39.7	39.7	39.7	25.9	25.9	25.9	25.9	25.9
Manure Feed Rate, Dry-Ash Free											
	kg/hr	12.4	12.4	12.7	12.7	12.7	12.7	8.26	8.26	8.26	8.26
	lb/hr	27.2	27.2	28.0	28.0	28.0	28.0	18.2	18.2	18.2	18.2
Air Feed Rate											
	k1/hr	1.40	1.40	4.25	4.25	4.25	4.25	0.765	0.765	0.765	0.765
	SCF/hr	49.5	49.5	150	150	150	150	27	27	27	27
Steam Feed Rate											
	kg/hr	3.09	3.09	2.72	2.72	2.72	2.72	3.72	3.72	3.72	3.72
	lb/hr	6.8	6.8	6	6	6	6	8.2	8.2	8.2	8.2
Particle Size, less than											
	cm	0.95	0.95	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32
	inch	3/8	3/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8
Raw Gas Production Rate											
	1/kg daf	0.536	0.527	0.680	0.705	0.705	0.761	0.468	0.268	0.237	0.306
	SCF/lb daf	8.59	8.44	(10.9)	(11.3)	(11.3)	(12.2)	7.5	4.3	3.8	4.9
Run Time With Manure, hr				2.1				2.1			

TABLE A-2
GAS COMPOSITION DATA
(All Compositions Are Mole Percent Rounded To First Decimal)

Component	RUN AND SAMPLE NUMBER										
	1-1	1-2	6a-1	6a-2	6a-3	6b-6	6b-7	7-2	7-3	8-3	
H ₂	23.1	27.4	28.7	21.6	23.9	19.0	21.0	29.0	27.4	19.2	
N ₂	22.2	7.1	15.2	28.7	33.0	17.2	12.9	20.6	25.7	29.9	
CH ₄	11.4	14.2	10.6	8.0	9.3	12.3	13.0	8.9	9.4	11.9	
CO	10.4	12.8	17.9	16.5	15.3	20.6	22.0	17.9	14.9	21.3	
CO ₂	29.3	32.3	20.8	18.9	16.2	22.6	21.7	16.0	14.9	11.1	
C ₂ H ₄	3.4	5.9	5.1	6.4	2.4	8.2	8.8	4.7	5.2	6.0	
C ₂ H ₆	0.2	0.4	1.8	0.7	-	-	0.7	2.9	2.6	0.6	
Avg. Mol. Wt.	25.8	24.4	22.7	24.6	23.3	25.2	24.5	22.0	23.2	23.3	
Total Energy, HHV											
kcal/l	2.64	3.51	3.48	2.99	2.43	3.59	3.97	3.45	3.34	3.42	
BTU/SCF	297	395	391	336	273	404	447	388	376	384	

TABLE A-2 (continued)
(All Compositions Are Mole Percent Rounded To First Decimal)

Component	RUN AND SAMPLE NUMBER									
	8-4	8-5	9-1	9-2	9-3	9-4	10-1	10-2	10-3	10-4
H ₂	17.6	15.4	14.7	11.5	16.3	17.7	22.1	20.1	20.4	21.0
N ₂	22.6	27.8	38.7	37.5	37.6	34.8	26.0	24.3	23.9	22.4
CH ₄	15.3	15.1	8.6	9.3	8.5	8.9	11.0	11.5	11.6	12.7
CO	22.4	19.7	19.5	20.6	19.7	20.5	21.1	23.2	23.5	21.9
CO ₂	15.7	15.4	13.7	15.8	13.6	13.6	14.3	14.9	14.6	15.5
C ₂ H ₄	5.7	5.8	4.2	4.7	3.9	4.0	5.2	5.4	5.5	6.0
C ₂ H ₆	0.8	0.7	0.5	0.6	0.4	0.5	0.3	0.6	0.6	0.5
Avg. Mol. Wt.	24.1	23.8	25.4	26.5	24.9	24.5	23.2	23.8	23.7	23.5
Total Energy, HHV										
kcal/l	3.67	3.50	2.57	2.66	2.56	2.68	3.18	3.41	3.35	3.50
BTU/SCF	412	394	289	299	288	301	358	373	377	394

TABLE A-3
TEMPERATURE PROFILE OF INDIVIDUAL RUNS
(All Values Are °C And Are Average Values)

REACTOR LOCATION/RUN	1	6a	6b	7	8	9	10
0 GAS INLET	300	300	300	300	300	300	300
1	565	720	625	660	570	845	595
2	740	815	690	690	685	860	680
3	825	845	735	690	740	840	735
4	875	845	780	730	770	825	765
5	860	890	840	785	835	845	815
6	930	915	865	825	865	845	815
7	930	895	860	815	840	845	775
8	855	820	765	730	765	690	775
9	720	670	630	595	625	-	635
10	590	560	520	490	515	485	525
11	460	405	370	365	355	380	385
12	425	365	355	355	325	370	365
13 GAS OUT	325	295	295	315	285	320	300
AVERAGE USING TRAPEZOIDAL RULE	711	694	641	617	629	668	628

APPENDIX B

A MODEL FOR REACTOR OPERATING CHARACTERISTICS

To highlight some of the operational features (not design) of the reactor discussed in the paper, a preliminary model is developed below. The model is based on several key assumptions or approximations which may not be entirely correct for design purposes of analysis of reactor dynamics, but will be sufficient for an assessment of operating features. The assumptions are noted where appropriate.

The basis for the model is the kinetic rate equation that has been used to describe the strict pyrolysis of manure particles, as developed by Young²⁹ and several other investigators for other cellulosics.⁴⁴ In the actual reactor, both pyrolysis and oxidation occur, but it is assumed that oxidation is complete within 30 to 60 cm of the air inlet (reactor bottom) because the feed air rate is much less than the stoichiometric quantity.⁴⁵ Thus, most of the reaction products of the top fed manure are assumed to be generated from pyrolysis.

For the assumed pyrolysis reaction, the rate equation is given by equations (1a) or (1b), using nomenclature similar to the above references:

$$\frac{dM}{dt} = -kM \quad (1a)$$

or

$$\frac{dX}{dt} = k(1-X) \quad (1b)$$

where M = mass of volatile or reactive manure, daf basis

k = rate constant = $k_0 e^{-E/RT}$

k_0 = pre-exponential factor, time^{-1}

E = energy of activation, cal/mole

R = gas-law constant, cal/mole, °K

T = absolute temperature, °K

X = mass conversion, mass of daf manure converted per unit mass of daf manure feed

t = time.

It is desirable, however, to express equation (1a) in terms of individual particles where N_p is the total number and M_p is the mass of an individual particle. Equation (1a) may then be written as equation (2).

$$\frac{d N_p M_p}{dt} = -k N_p M_p \quad (2)$$

If N_p is assumed to be constant (i.e., no break-up or agglomeration of particles), then using the volume of a particle, V_p , and assuming all particles are the same size, equation (2) may be written

$$\frac{1}{V_p} \frac{d M_p}{dt} = -k C_m \quad (3)$$

where C_m = concentration of reactive mass per unit volume of particles; $C_m = M_p/V_p$.

Equation (3) or (4) represents a definition of reaction rate of a manure particle using the particle volume as the reaction volume⁴⁵; that is,

$$r_m = \frac{1}{V_p} \frac{d M_p}{dt} \quad (4)$$

where r_m = reaction rate based on particle volume.

It is noted, at this point, that it is not necessary to assume that the particle volume, V_p , is a constant.

To describe the pyrolysis reaction occurring, a differential cylinder at any point in the reactor may be chosen. Then a steady-state material balance may be written as follows:

$$(-R_m) (d V_r) = F_{mo} dX \quad (5)$$

where R_m = rate of reaction based on reactor volume

V_r = reactor volume

F_{mo} = feed rate of daf manure, lb/hr.

For a constant number of particles, N_p , the relationship between R_m and r_m is:

$$R_m = \frac{1}{V_r} \frac{d M_p N_p}{dt}, \quad (6a)$$

$$= (V_p N_p / V_r) r_m, \quad (6b)$$

$$= \gamma r_m. \quad (6c)$$

The term $\gamma = N_p V_p / V_r$ is the volume fraction of particles existing in the reactor at any point. Combining equations (6c) and (5), one can develop

$$(C_{mo} \gamma / F_{mo}) d V_r = -(1/k) d (\ln C_m) \quad (7)$$

where C_{mo} = initial (or feed) concentration of reactive manure per unit particle volume.

The development of equation (7) requires that V_p be considered a constant. This assumption is probably not a good assumption for conversion levels exceeding 80 percent, but does appear to be a reasonable approximation up to this level, especially considering the high fraction of ash in manure (20-25 percent; 29). The assumption of constant V_p permits equations (8) and (9) to be used in developing equation (7).^{*} The term, F_m , is the feed rate which corresponds to the particle concentration, C_m ,

$$X = 1 - C_m / C_{mo} \quad (8)$$

$$C_m / C_{mo} = F_m / F_{mo} = M_p / M_{po} \quad (9)$$

in the reactor at any given point. Equation (7) may be integrated directly to obtain a result which is descriptive of a general tubular reactor containing a first order reaction. This result is given by equation (10), assuming that an average value of the product of the rate constant and the volume fraction can be defined.

$$(\overline{\gamma k}) C_{mo} V_r / F_{mo} = -\ln (C_m / C_{mo}) \quad (10)$$

where $(\overline{\gamma k}) = [\gamma k d V_r] / V_r$.

When γ is constant and the reaction is isothermal, the left-hand side of equation (10) can be rearranged to yield, after dividing by k :

^{*}The last equality in equation (9) does not require the assumption of constant volume; N_p must, however, be constant.

$$\tau' = \gamma C_{mo} V_r / F_{mo} = N_p M_{po} / F_{mo} \quad (11)$$

where τ' is the residence time for the ideal case of constant γ and k as noted. However, equation (10) demonstrates that τ' is only an apparent value for the current reactor design because temperature was not constant and γ is not expected to remain constant.

A closer approximation to the actual τ would be to define a term $(\bar{k}) \tau$ and assume that $(\bar{k}\bar{\gamma}) = (\bar{k})(\bar{\gamma})$ so that:

$$\tau = \bar{\gamma} C_{mo} V_r / F_{mo} \quad (12)$$

In other words, the actual residence time will depend upon the flow regime(s) in the reactor, through $\bar{\gamma}$. This result is not unexpected, but it must be appreciated because the product distribution could also be altered by a change in $\bar{\gamma}$. In equation (11), the rigorous average value also demonstrates the close association between reaction temperature and particle distribution within a reactor using a solid feedstock with these kinetics. It also suggests a reason for part of the differences in product distribution, at constant $C_{mo}V_r/F_{mo}$, between the tubular reactor developed here and that of a fluidized bed or that of a similar tubular reactor with co-current flow.^{39, 44} It is also important to realize that no attempt has yet been made to alter the flow regime in the reported reactor which would change $\bar{\gamma}$, and potentially alter the product rate and/or distribution.

The volume fraction term (or $1-\epsilon$, where ϵ is the void fraction) can be used to illustrate a probable limiting factor of the reactor operation: heat transfer to the particle. At the temperatures involved, radiation to a particle is probably the dominant mechanism.⁴⁴ Thus, there probably exists a critical $\bar{\gamma}$, $\bar{\gamma}_c$, beyond which the expected or desired X can no longer be achieved, as the reactor is now operated. Or, at values of $\bar{\gamma}$ greater than $\bar{\gamma}_c$, all particles will not be exposed to the same radiant energy transfer from the wall. In this case, interparticle radiant energy transfer (or perhaps conduction/convection, if the volume fraction approaches that of a packed bed) would become a key factor. It may be argued that the effect of $\bar{\gamma}$ would simply be reflected in the measured temperature. However, the point being discussed here is that an average temperature can probably be imposed (or held constant over a range of $\bar{\gamma}$) and that X may still be altered due to the change in heat transfer from the wall surface case to interparticle effects. Over the three-fold range of feed rates explored to date, this potential limitation does not appear to have been approached.

The $\bar{\gamma}$ effect also suggests that the reactor performance may depend upon the manner in which the reactor is started up. For example, if a large inventory of solids is allowed to accumulate in the reactor before solids discharge is matched to solids feed, a significant bed (large $\bar{\gamma}$) could exist at steady-state which would reduce heat transfer to particles as discussed above and thereby affect X . Again, this limit does not appear to have occurred as the reactor is currently operated, over the range of data explored.

Young²⁹ has also shown that at a given level of conversion over a wide range of heating rates (50°C/min to 1000°C/min), a certain fraction (δ) of the mass loss will always exist as a low molecular weight gas (boiling point less than 25°C at 1 atm) when the fluid phase residence time is generally less than 2 seconds. Because the operation of the pilot-scale reactor approximates these conditions, a similar effect may be expected. The gas fraction obtained from the reactor may then be expressed in terms of the δ -fraction as follows:

$$\delta X = \delta \frac{M_{po} - M_p}{M_{po}} = \frac{M_G}{M_{po}} = \frac{F_G}{F_{mo}} \quad (13)$$

where M_G = mass (or SCF) of gas produced

F_G = flow rate of gas produced.

This result serves to illustrate that F_G/F_{mo} is a correct correlation variable which is independent of particle volume assumptions. For this reason, the gas yield has been expressed as standard ℓ per kg daf manure feed in Figure 7 of the text. A similar analysis may be used to demonstrate that any fraction of the produced gas should be expressed on a similar basis, as done in Figures 8 and 9.